For Reference

NOT TO BE TAKEN FROM THIS ROOM

Ex libris
universitatis
albertaensis

For Reference

NOT TO BE TAKEN FROM THIS ROOM

The University of Alberta
Printing Department
Edmonton, Alberta

THE UNIVERSITY OF ALBERTA

RACEMIZATION AND SOLVOLYSIS OF SULFONIUM SALTS AND SULFONIUM YLIDES

BY

© RALPH L. TOMILSON

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE
OF MASTER OF SCIENCE

DEPARTMENT OF CHEMISTRY
EDMONTON, ALBERTA JUNE, 1968

Thesis
1968 1F
224

THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES

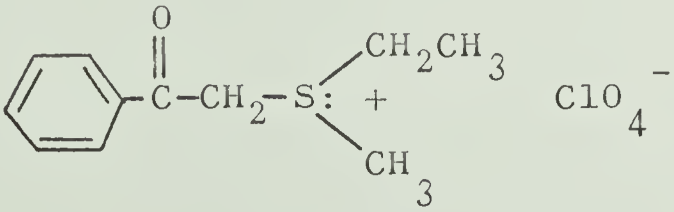
The undersigned certify that they have read and recommend to the Faculty of Graduate Studies for acceptance a thesis entitled "Racemization and Solvolysis of Sulfonium Salts and Sulfonium Ylides" submitted by Ralph L. Tomilson, B. Sc., in partial fulfillment of the requirements for the degree of Master of Science.

ABSTRACT

The racemization and solvolysis of phenacylethylmethylsulfonium perchlorate (I) were investigated.

Optically active I was obtained by synthesizing the (-)-dibenzoylhydrogentartarate salt and separating the diastereomers, followed by replacement of the anion by perchlorate. Compound I racemizes 600 times faster than it solvolyzes at 70° in methanol. The loss of optical activity is due to racemization and not decomposition of the substrate. Solvolysis of I results in the formation of 2-methylthioacetophenone (phenacyl methyl sulfide) and 2-ethylthioacetophenone (phenacyl ethyl sulfide), in the amounts of 47 and 18 mole per cent respectively, plus 35 mole per cent unidentified products.

Mechanisms which would account for racemization of phenacylethylmethylsulfonium perchlorate without decomposition were considered. The only mechanism which could account for this, as well as the rate difference between solvolysis and racemization and the observed products of solvolysis is pyramidal inversion about the central sulfur atom. This is analogous to the inversion of an ammonia molecule.



I

Digitized by the Internet Archive
in 2020 with funding from
University of Alberta Libraries

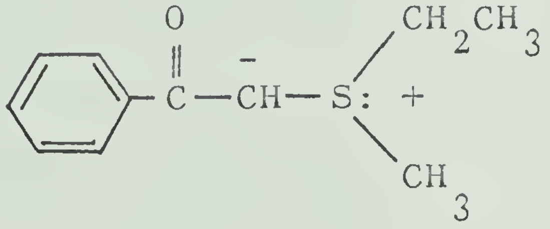
https://archive.org/details/Tomilson1968

The racemization and decomposition of ethylmethylsulfonium phenacylide (II) were investigated.

Optically active II was obtained by treatment of optically active I with base, followed by workup. This is the first reported synthesis of an optically active sulfonium ylide. Compound II racemizes ca. 100 times faster than it solvolyzes. Loss of optical activity is due to racemization and not decomposition of the substrate. Decomposition of II results in the formation of 67 mole per cent of 2-methylthioacetophenone (decomposition studied in CCl_4 at 50°).

The only reasonable mechanism to account for racemization of II is pyramidal inversion about the central sulfur atom, analogous to the inversion of I.

A discussion of the relative rates of racemization of sulfonium salts, sulfonium ylides and aryl sulfoxides is given.



II

ACKNOWLEDGEMENT

The writer wishes to express appreciation and gratitude to:

Dr. David Darwish, Research Director, for his patience and understanding, and for his insight and guidance throughout the course of this project.

Mr. J. Hoyle and Mrs. M. Tchaikowsky, who displayed patience so many times when samples were submitted for n.m.r. analyses at inopportune times.

Mr. B. Altenkirk and Mr. L. Ball, for their many suggestions and for their aid during the course of product analyses by thin layer chromatography.

Past and present members of the research group for their suggestions and discussions concerning the project.

The faculty and technical staff of the Department of Chemistry for their interest and encouragement.

The University of Alberta and the National Research Council for financial support.

TABLE OF CONTENTS

		Page
INTRODUCTION		1
CHAPTER I	Phenacylethylmethylsulfonium salts	7
	Solvolysis studies	8
	Racemization studies	23
	Product analyses	30
	Discussion	32
	Activation parameters	37
	Experimental	39
CHAPTER II	Ethylmethylsulfonium phenacylide	67
	Racemization studies	69
	Decomposition studies	72
	Discussion	72
	Activation parameters	79
	Experimental	86
BIBLIOGRAPHY		92

LIST OF TABLES

Page

Table I — Solvolysis of 0.0200 M pheancylethylmethylsulfonium perchlorate in anhydrous methanol at 90.00° Run 1-167 — 14

Table II — Solvolysis of 0.0200 M phenacylethylmethylsulfonium perchlorate in anhydrous methanol at 90.00° Run 1-292 — 16

Table III — Solvolysis of 0.0200 M phenacylethylmethylsulfonium perchlorate in anhydrous methanol at 90.00° with added 2,6-lutidine (0.0600 M) Run 2-11 — 18

Table IV — Solvolysis of phenacylethylmethylsulfonium perchlorate in anhydrous methanol (k_t obtained from slope of log (a-x) vs time plot) — 22

Table V — Solvolysis of phenacylethylmethylsulfonium perchlorate (0.0200 M) in anhydrous methanol at 90.00° with added 2,6-lutidine (0.1013 M) and added 2,6-lutidinium perchlorate (0.0987 M) Run 2-50 — 20

Table VI — Racemization of 0.0200 M (-)-phenacylethylmethylsulfonium perchlorate in anhydrous methanol at 50.00° with added perchloric acid (2.99×10^{-3} M) Run 1-249 — 24

Table VII — The racemization of phenacylethylmethylsulfonium perchlorate under various conditions — 29

Page

Table VIII Standard solutions for the product analysis of the methanolysis of phenacylethylmethylsulfonium perchlorate 54

Table IX Control solutions for the product analysis of the methanolysis of phenacylethylmethylsulfonium perchlorate 55

Table X Control analyses of the products of methanolysis of phenacylethylmethylsulfonium perchlorate 56

Table XI Standard solutions for the product analysis of the methanolysis of phenacylethylmethylsulfonium perchlorate with added 2,6-lutidine 58

Table XII Control solutions for the product analysis of the methanolysis of phenacylethylmethylsulfonium perchlorate with added 2,6-lutidine 59

Table XIII Control analyses of the products of methanolysis of phenacylethylmethylsulfonium perchlorate with added 2,6-lutidine 60

Table XIV Racemization of 0.044 M (-)-ethylmethylsulfonium phenacylide in carbon tetrachloride at 25.00° Run 1-215 73

Table XV Racemization of (-)-ethylmethylsulfonium phenacylide in various solvents at 25.00° and 50.00° using an incident light wavelength of 589 mμ 75

Table XVI Nuclear magnetic resonance spectral data for ethylmethylsulfonium phenacylide and dimethylsulfonium phenacylide 76

LIST OF FIGURES

		Page
Figure I	Diagrammatic representation of the inversion of SR_3^+ by gradually increasing the amplitude of the symmetrical deformation vibrations	1
Figure II	Potential energy, V, for the inversion of the pyramid SR_3^+ vs bond angle, α.	2
Figure III	Formation of phenacylethylmethylsulfonium salts	9
Figure IV	Specific rotation of (-)-phenacylethylmethylsulfonium perchlorate vs wavelength of the incident light, in solvent methanol	10
Figure V	Solvolysis of 0.0200 M phenacylethylmethylsulfonium perchlorate in anhydrous methanol at 90.00° Run 1-167	15
Figure VI	Solvolysis of 0.0200 M phenacylethylmethylsulfonium perchlorate in anhydrous methanol at 90.00° Run 1-292	17
Figure VII	Solvolysis of 0.0200 M phenacylethylmethylsulfonium perchlorate in anhydrous methanol at 90.00° with added 2,6-lutidine (0.0600 M) Run 2-11	19
Figure VIII	Solvolysis of 0.0200 M phenacylethylmethylsulfonium perchlorate in anhydrous methanol at 90.00° with added 2,6-lutidine (0.1013 M) and added 2,6-lutidinium perchlorate (0.0987 M) Run 2-50	21

Page

Figure IX Racemization of 0.0200 M (-)-phenacylethylmethylsulfonium perchlorate at 50.00° in anhydrous methanol in the presence of perchloric acid (2.99×10^{-3} M) Run 1-249 25

Figure X Calibration curve for the product analysis of phenacylethylmethylsulfonium perchlorate in anhydrous methanol, using ethyl phthalate as internal standard Run 2-35 57

Figure XI Calibration curve for the product analysis of the methanolysis of phenacylethylmethylsulfonium perchlorate with added 2,6-lutidine Run-219 61

Figure XII Synthesis of ethylmethylsulfonium phenacylide 70

Figure XIII Specific rotation of (-)-ethylmethylsulfonium phenacylide vs wavelength of incident light (Solvent: benzene) 71

Figure XIV Racemization of 0.044 M (-)-ethylmethylsulfonium phenacylide in carbon tetrachloride at 25.00° Run 1-215 74

INTRODUCTION

The ammonia molecule is capable of undergoing a pyramidal inversion about the nitrogen atom. The potential barrier restricting this inversion was calculated by Manning (1), using data on the hyperfine splitting of certain lines in its infrared and microwave spectra. This method of calculating the potential barrier restricting such an inversion in other pyramidal molecules cannot be applied, since the necessary spectral data are not available in the literature.

Kincaid and Henriques (2) were able to calculate the activation energy for the intramolecular inversion of a number of pyramidal molecules, including the trimethylsulfonium ion. They chose a pyramidal model of the sulfonium ion and assumed that its inversion merely required the gradual increase of the symmetrical deformation vibrations as shown in Figure I.

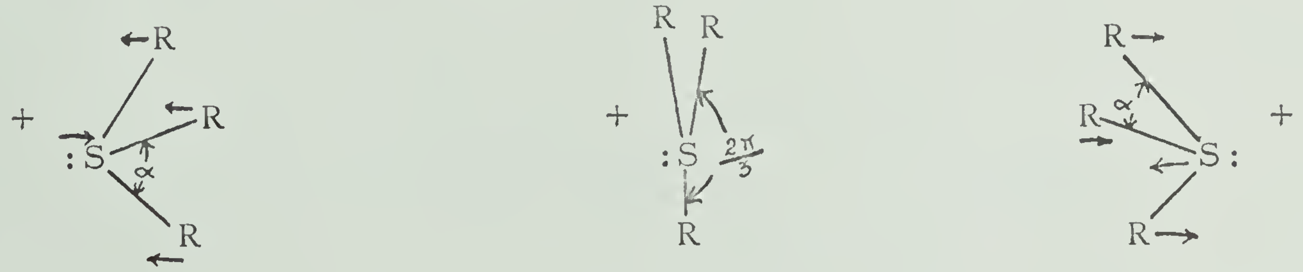


Figure I. Diagrammatic representation of the inversion of SR_3^+ by gradually increasing the amplitude of the symmetrical deformation vibrations.

By using the force constants controlling this vibration,

a plot as shown in Figure II can be made; a double parabolic function of the form V = A $(\Delta\alpha)^2$ on either side of the planarconfiguration.

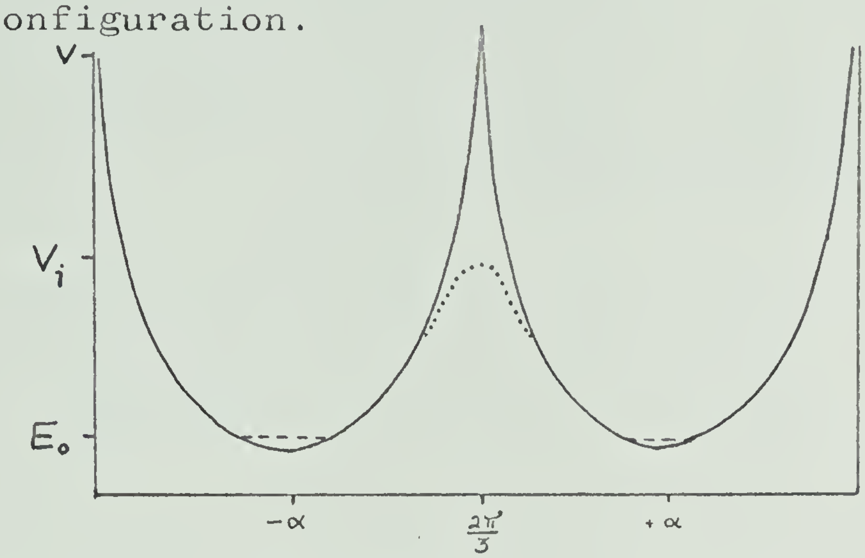


Figure II. Potential energy , V , for the inversion of the pyramid SR_3^+ vs bond angle , α . The solid line represents the parabolic function of Kincaid and Henriques (2) ; the broken line represents the valence force field function of Weston (4).

Using the parabolic function shown below, which was suggested by Wall and Glocker (3), Kincaid and Henriques obtained a value of 100 kcal/mole for the activation energy required for the intramolecular inversion of the trimethylsulfonium ion.

$$V = \frac{1}{2} k \left(|x| - |x_o| \right)^2$$

x = distance of S from the plane of the R groups

x_o= the distance at equilibrium

k = the force constant , $k = 4\pi^2 \nu_3^2 \mu$

μ = reduced mass

ν_3 = the vibrational frequency

For the trimethylsulfonium ion they used the following values:

1.82 Å = C-S bond length
109.5° = C-S bond angle (an upper limit; lower values make the activation energy higher)
0.61 Å = the equilibrium height
600 cm^{-1} = vibrational frequency (a lower limit; for dimethyl sulfide frequency is 648 cm^{-1}; higher values increase the calculated energy).

Their value of 100 kcal/mole is so high that "flipping" of the trimethylsulfonium ion would be an unobservable process. The authors pointed out that this parabolic function tends to overestimate the value for the inversion energy. As an example, this method predicts a value for ammonia that is 50 per cent higher than the accepted value. But even a 50 per cent reduction in value for the trimethylsulfonium ion still suggests that its inversion would be too slow to detect.

Weston (4) has made a more recent estimate for the activation energy by applying the valence force field function of Costain and Sutherland (5) to the double minima problem.

$$V_{(\alpha)} = \frac{3}{2}\left\{k_1\ (\Delta \ell)^2 + k_\alpha(\Delta\alpha)^2\right\}$$

where k_1 = C-S bond stretching force constant

k_α = the bond bending force constant

Δl = change in bond length from equilibrium value

$\Delta\alpha$ = change in bond angle from equilibrium value

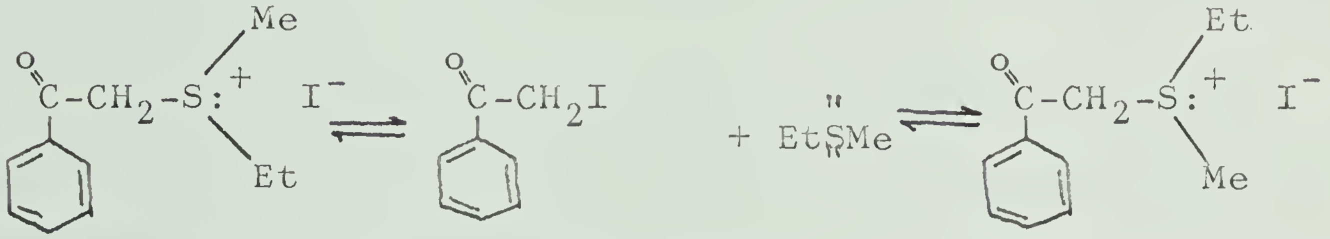
Using symmetry coordinates involving ν_1 and ν_2 they related Δl to $\Delta\alpha$ and obtained

$$V_i = K\left[(2\pi/3) - \alpha\right]^2$$

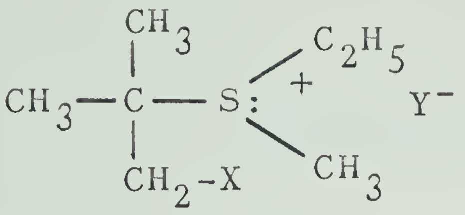
Assuming the following values, 1.82 Å for the bond length, 654 and 285 cm^{-1} for the vibrational frequencies, 109.5° for the bond angle, Weston obtained an activation energy of 16.5 kcal/mole; assuming a bond angle of 100° by anology to trimethyl phosphine gave a value of 24.1 kcal/mole. The author pointed out that his values were surprisingly low and suggested that this may be due to using force constants that are not corrected for vibrational anharmonicity.

Weston knew that his values were too low since they would indicate that active sulfonium salts could not be obtained at room temperature, whereas optically active sulfonium salts had been known since 1900 when Pope and Peachy (6) resolved carboxymethylethylmethylsulfonium d-bromocamphorsulfonate. In the same year Smiles (7) resolved phenacylethylmethylsulfonium d-bromocamphorsulfonate and converted each optically active isomer into the corresponding picrate.

The first study of the racemization of optically active sulfonium salts was made in 1930 by Kenyon et al (8). Using phenacylethylmethylsulfonium iodide they concluded that racemization involved a nucleophilic displacement on the methylene carbon of the phenacyl moiety by halide ion to form inactive phenacyl iodide and dimethyl sulfide, followed by recombination to form the racemic salt as shown below.



It was not until 1966 that it was shown that optically active sulfonium salts could racemize without decomposition. In that year Darwish and Tourigny (9) found that t-butylethylmethylsulfonium salts racemized more rapidly than they decomposed. This was found to be true in a variety of solvents. By introducing substituents into the |-position of the t-butyl moiety and observing their effects on the rates of racemization and solvolysis, they found that the racemization rate was enhanced regardless of the electronic effect of the particular substituent involved. The solvolysis rate, on the other hand, was enhanced by electron-donating substituents and retarded by electronwithdrawing substituents.



I $X = H$

II $X = OCH_3$

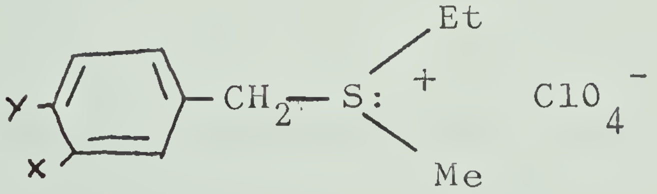
III $X = CH_3$

IV $X = C_6H_5$

As a result they were able to show that the major portion of the racemization involved a pyramidal inversion about the central sulfur atom, analogous to the inversion of an ammonia molecule.

Mislow and Scartazzini (10) have shown that this mechanism accounts for the racemization of the 1-adamantylethylmethylsulfonium system.

A study has also been made of the benzylethylmethylsulfonium system by Darwish and Hui (11). By introducing substituents into the para- and/or meta- positions and studying their effects on the rates of solvolysis and racemization, they were able to show once again that the major portion of the racemization is accounted for by a pyramidal inversion about the central sulfur atom.



I $X = H$ $Y = H$

II $X = H$ $Y = NO_2$

III $X = NO_2$ $Y = OCH_3$

To further study the importance of pyramidal inversion in the racemization of optically active sulfonium salts, we have undertaken a study of the phenacylethylmethylsulfonium system.

CHAPTER I

PHENACYLETHYLMETHYLSULFONIUM SALTS

This chapter describes the synthesis and resolution of phenacylethylmethylsulfonium salts. The kinetics of the racemization and solvolysis and the solvolysis products will also be discussed. In addition, the ratio of solvolysis to racemization rates and solvent and temperature effects will be discussed.

SYNTHESIS AND RESOLUTION

Figure III outlines the route which was followed for the synthesis and resolution of phenacylethylmethylsulfonium perchlorate. Ethyl methyl sulfide readily reacts with phenacyl bromide to form the sulfonium bromide salt. The reaction and workup should be carried out in the dark to prevent formation of bromine. Exchange of the sulfonium salt anion was accomplished by converting it to the hydroxide using a Dowex 1-X8 anion exchange resin, in its hydroxide form, and neutralizing the sulfonium hydroxide with the appropriate acid. Optically active phenacylethylmethylsulfonium perchlorate was obtained via the (-)-2R,3R-dibenzoylhydrogentartarate salt. The sulfonium hydroxide was neutralized with (-)-2R,3R-dibenzoyltartaric acid monohydrate and after separation of the diastereomers, the less soluble diastereomer was converted to the levorotary

perchlorate salt. The dextrorotary salt was not obtained. All compounds gave satisfactory analyses. These, as well as melting point, nuclear magnetic resonance spectra and infrared spectra are reported with the detailed synthetic procedure in the Experimental section. All the data are consistent with the assigned structures. The sulfonium bromide exhibits non-equivalence of the methylene protons of both the ethyl and phenacyl moieties in its n.m.r. spectrum. This behaviour is expected since the groups are adjacent to an assymmetric center. The other sulfonium salts, also potential candidates to exhibit this behaviour, did not show non-equivalence of the abovementioned protons. The change in specific rotation with change in wavelength of the incident light for (-)-phenacylethylmethylsulfonium perchlorate is illustrated in Figure IV.

SOLVOLYSIS STUDIES

The rate of solvolysis of phenacylethylmethylsulfonium perchlorate was studied by two methods, by following the rate of appearance of acid and by following the rate of disappearance of starting material by means of nuclear magnetic resonance spectroscopy. The data are summarized in Table IV. The titrimetric method gave only 65 per cent of the theoretical infinity titer and resulted in a drifting rate constant, k_t. The rate constants were calculated

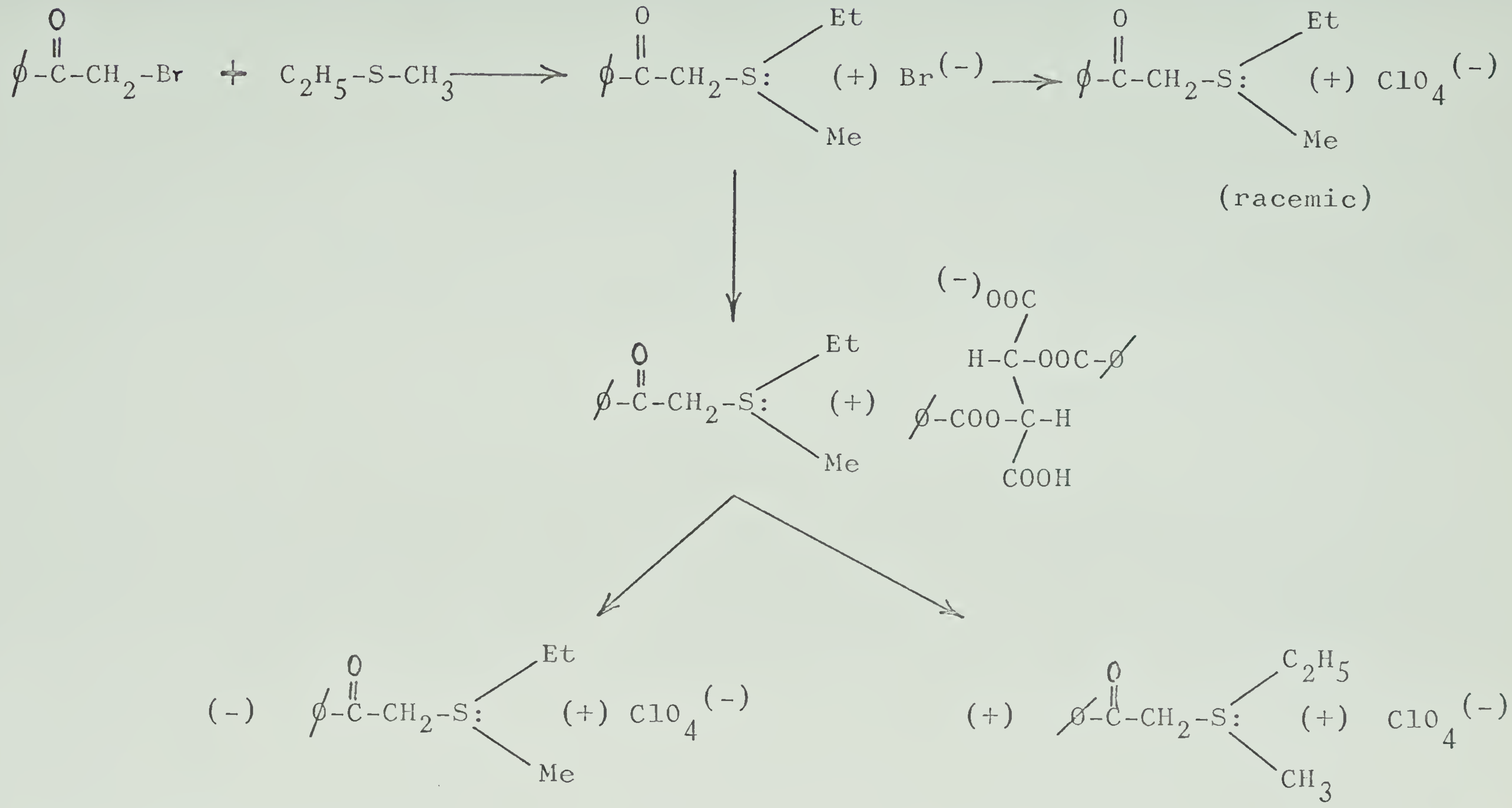


Figure III. Formation of Phenacylethylmethylsulfonium Salts

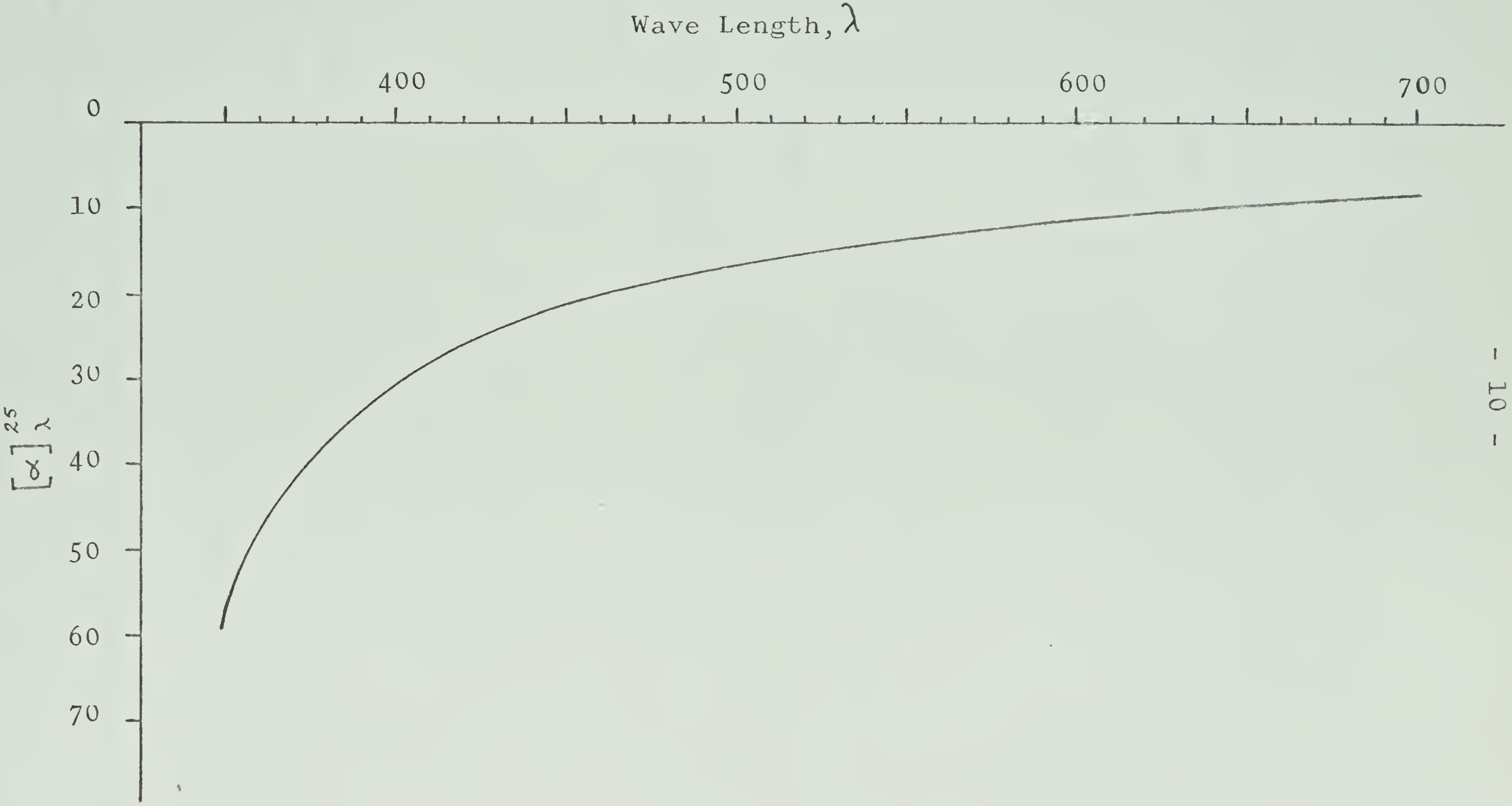


Figure IV. Specific rotation of (-)-phenacylethylmethylsulfonium perchlorate vs wavelength of the incident light, in solvent methanol.

from the relationship:

$$k_t = \frac{2.303}{t} \log \frac{V_\infty - V_o}{V_\infty - V_t}$$

where V_∞ is the theoretical infinity titer and V_t is the titer at time t. A typical titrimetric rate analysis, Run 1-167, is shown in Table I with the corresponding plot of log ($V_\infty - V_t$) vs time shown in Figure V. The titrimetric rate constants reported in Table IV are obtained from the initial slope of the log ($V_\infty - V_t$) vs time plot.

The solvolytic rate study using n.m.r. spectroscopy, Run 1-292, with ethylene carbonate as internal standard, clearly showed that no starting material remained after 10 half-lives of solvolysis. This indicates that the incomplete acid titer obtained in the titrimetric rate determination is due to consumption of the acid in a side reaction and not to a reversible solvolysis reaction. The rate constant for this reaction was obtained from the slope of the plot of log (a - x) vs time, where (a - x) is the concentration of phenacylethylmethylsulfonium perchlorate at time t. The rate analysis for this run is shown in Table II with the corresponding plot of log (a - x) vs time illustrated in Figure VI. Due to the method employed, this analysis is subject to a very large error.

A solvolytic rate study in the presence of added 2,6-lutidine was made by employing n.m.r.spectroscopy (Run 2-11). The rate constants, k_t, were calculated from

the relationship:

$$k_t = \frac{2.303}{t} \log \frac{a}{a - x}$$

where a is the initial concentration and (a - x) is the concentration at time t of phenacylethylmethylsulfonium perchlorate. The rate analysis for this study is shown in Table III with the corresponding plot of log (a - x) vs time shown in Figure VII. A drifting rate constant was again observed; the rate constant reported in Table IV was obtained from the initial slope of the log (a - x) vs time plot. It can be seen that the reaction in the presence of 2,6-lutidine is considerably faster than in its absence.

The rate was also measured by n.m.r. spectroscopy in the presence of a five fold molar excess of 2,6-lutidine and a five fold molar excess of 2,6-lutidinium perchlorate (Run 2-50). The rate constants for this reaction were calculated in the same manner as above. The reaction was followed to 75 per cent completion, and a good straight line was obtained when a plot of log (a - x) vs time was made. The rate analysis of this study is shown in Table V, with the corresponding plot of log (a - x) vs time shown in Figure VIII. This reaction is only slightly faster than the reaction involving the sulfonium salt alone, and is considerably slower than the reaction in the presence of 2,6-lutidine only.

The decomposition in the presence of 2,6-lutidine may be the decomposition of the ylide and not the sulfonium salt. Since the ylide would result from the following equilibrium,

$$\text{Salt} + :\text{B} \rightleftharpoons \text{Ylide} + \text{BH}^+$$

The fraction of material in the form of ylide will be governed by the following equation:

$$\text{Keq} = \frac{[\text{Ylide}]\ [\text{BH}^+]}{[\text{Salt}]\ [:\text{B}]}$$

$$\text{and} \quad \frac{[\text{Ylide}]}{[\text{Salt}]} = \text{Keq}\ \frac{[:\text{B}]}{[\text{BH}^+]}$$

As the reaction proceeds, the ratio $\frac{[:\text{B}]}{[\text{BH}^+]}$ decreases. Hence, the fraction of the material in the form of ylide decreases, and the rate also decreases.

In the buffered solution, the ratio $\frac{[:\text{B}]}{[\text{BH}^+]}$ is very small and is essentially constant. The fraction of the material in the form of ylide will also be very small. In fact, by a comparison of the rates of solvolysis of the sulfonium salt with and without added buffer it appears that the buffer almost eliminates ylide formation.

Alternatively the faster solvolysis rate in the presence of base may be due to removal of a proton from the solvent, thereby creating a better nucleophile. If this is the case, then a similar argument applies.

TABLE I

SOLVOLYSIS OF 0.002 M PHENACYLETHYLMETHYLSULFONIUM PERCHLORATE IN ANHYDROUS METHANOL AT 90.00° RUN 1-167

Aliquot: 5.008 ml. Titrant: NaOMe (0.035 M)

Indicator: Bromphenol Blue Theoretical Infinity Titer: 2.814 ml.

Time (10^5 sec)	V_t (ml.)	Log ($V_\infty - V_t$)	$10^7 k_t$ (sec^{-1})
0	0.000	.44932	
0.864	0.201	.41714	9.60
1.764	0.435	.37639	9.56
2.637	0.601	.34498	9.12
3.789	0.775	.30942	8.51
4.275	0.871	.28847	8.67
4.671	0.902	.28149	8.26
5.427	0.970	.26576	7.78
6.282	1.052	.24601	7.46
7.128	1.163	.21775	7.48
10.845	1.404	.14922	6.36
11.763	1.483	.12418	6.37

From graph : $k_t = 9.1 \times 10^{-7}$

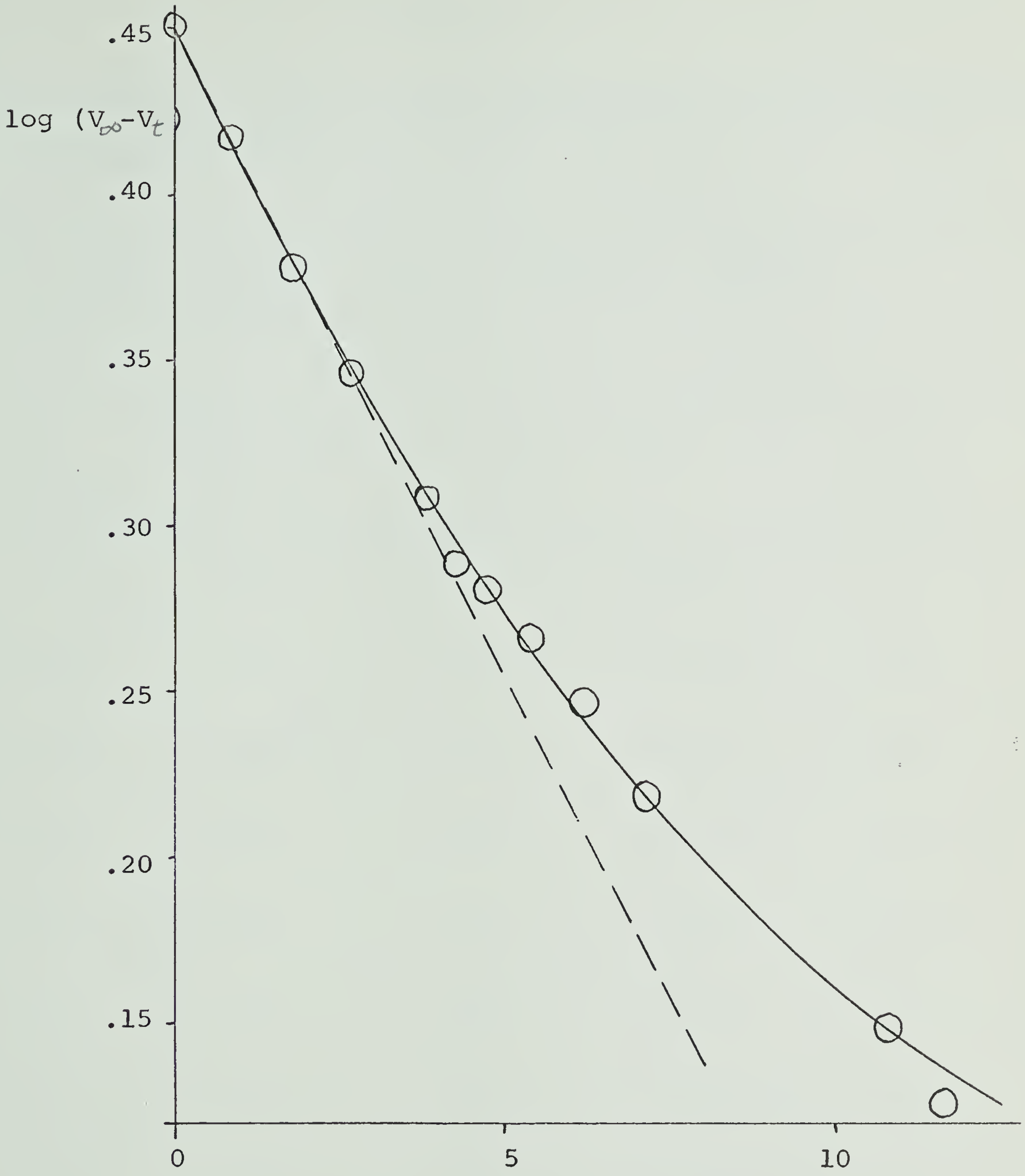


Figure V. Solvolysis of 0.0200 M phenacylethylmethylsulfonium perchlorate in anhydrous methanol at 90.00° Run 1-167

TABLE II

SOLVOLYSIS OF 0.0200 M PHENACYLETHYLMETHYLSULFONIUM PERCHLORATE IN ANHYDROUS METHANOL AT 90.00° RUN 1-292

Internal Standard: Ethylene carbonate (0.4007 M)

Varian A-60 NMR Spectrometer

Time (10^5sec)	Integration (τ 4.5)	Integration (Int. Std.)	Log (a - x)	10^7 k_t (sec^{-1})
0	17.5	37.5	$\bar{1}.6690$	
2.61	14.0	33.9	$\bar{1}.6160$	4.68
3.60	23.8	66.7	$\bar{1}.5524$	7.46
5.53	19.5	64.0	$\bar{1}.4839$	7.70
6.91	10.1	36.5	$\bar{1}.4420$	7.56
8.64	9.2	36.7	$\bar{1}.3992$	7.19
13.07	12.3	60.5	$\bar{1}.3081$	6.36
18.25	11.8	68.0	$\bar{1}.2393$	5.42

From graph : $k_t = 9.0 \times 10^{-7}$

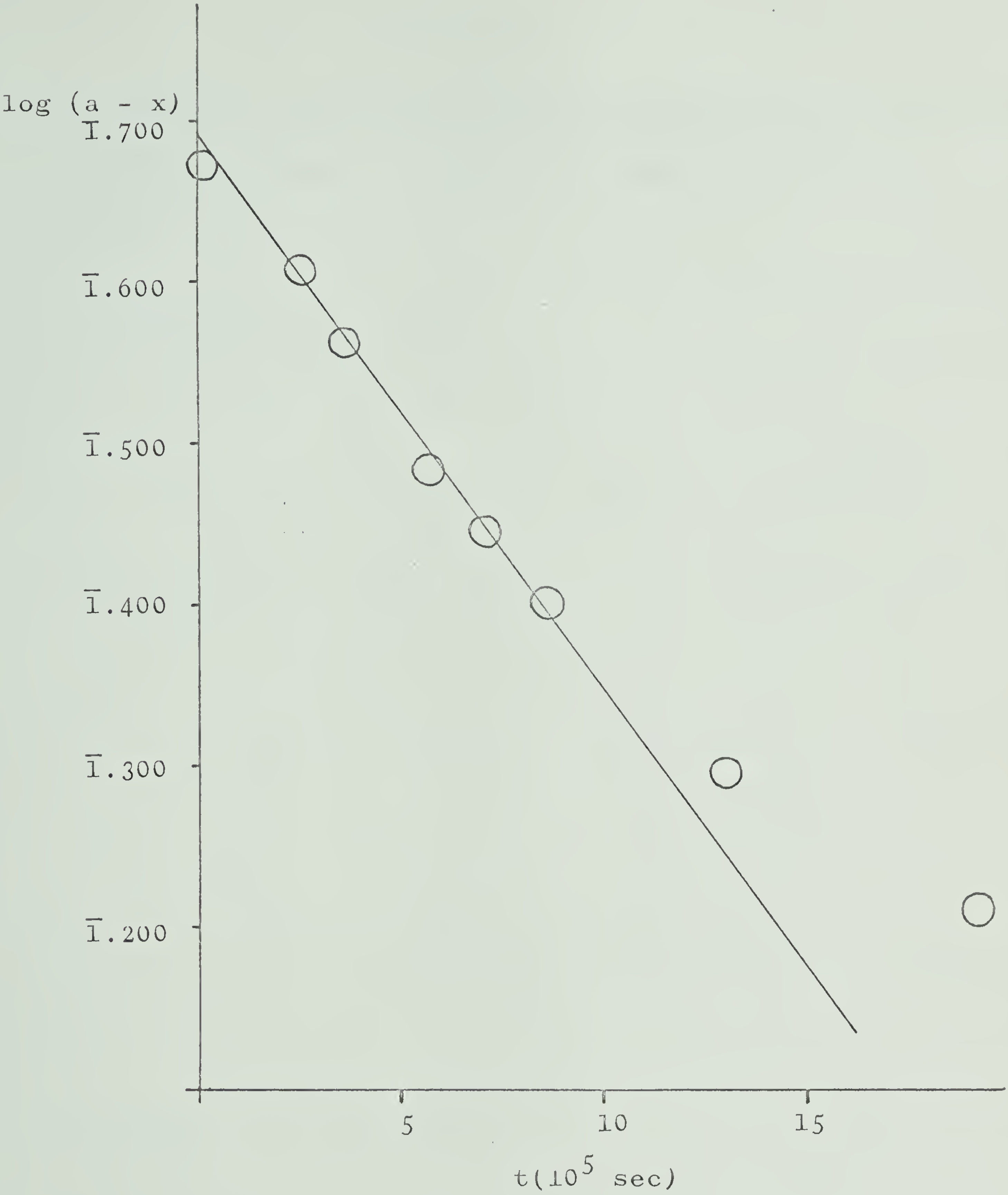


Figure VI. Solvolysis of 0.0200 M phenacylethylmethylsulfonium perchlorate in anhydrous methanol at 90.00° Run 1-292

TABLE III

SOLVOLYSIS OF 0.0200 M PHENACYLETHYLMETHYLSULFONIUM PERCHLORATE IN ANHYDROUS METHANOL AT 90.00° WITH ADDED 2,6-LUTIDINE (0.0600 M) RUN 2-11.

Varian A-60 NMR Spectrometer

Internal Standard : Ethylene carbonate (0.4007 M)

Time (10^4sec)	Integration (τ 4.5)	Integration (Int. Std.)	[Salt] (a-x)	Log [Salt] log(a-x)	10^6 k_t (sec^{-1})
0	35.1	73.4	.0200	$\bar{2}.3013$	
3.87	33.0	93.0	.0150	$\bar{2}.1761$	7.46
7.83	33.0	126.0	.01096	$\bar{2}.0398$	7.67
9.63	17.1	72.2	.00991	$\bar{3}.9961$	7.30
12.15	23.2	106.5	.00912	$\bar{3}.9598$	6.49
15.93	7.4	39.8	.00778	$\bar{3}.8910$	5.96
18.81	8.9	52.9	.00704	$\bar{3}.8475$	5.56
250.56	0				

From graph : $k_t = 7.7 \times 10^{-6}$

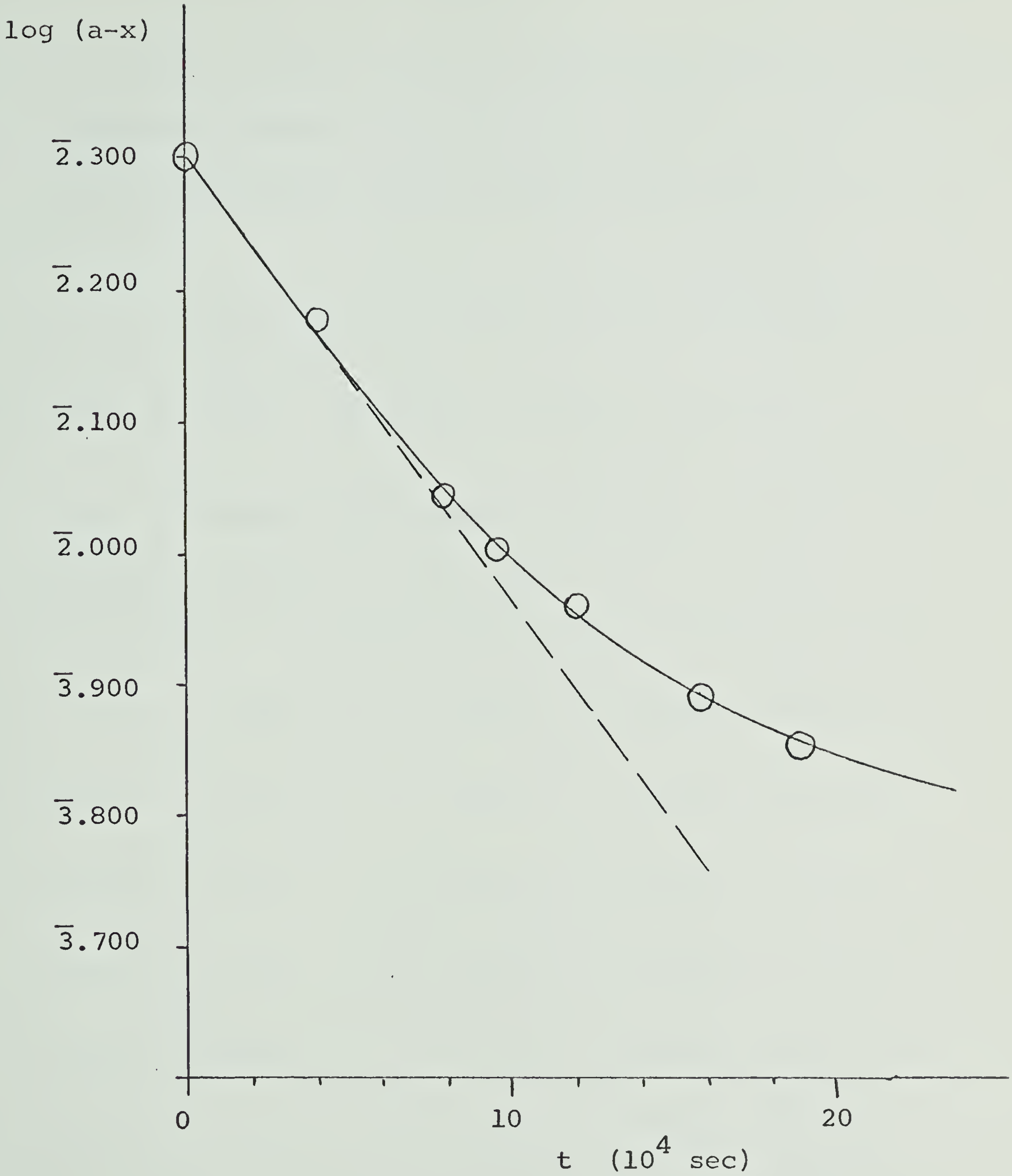


Figure VII. Solvolysis of 0.0200 M phenacylethylmethylsulfonium perchlorate at 90° in anhydrous methanol with added 2,6-lutidine (0.0600 M) Run 2-11

TABLE V

SOLVOLYSIS OF 0.0200 M PHENACYLETHYLMETHYLSULFONIUM PERCHLORATE IN ANHYDROUS METHANOL AT 90.00° WITH ADDED 2,6-LUTIDINE (0.1013 M) AND ADDED 2,6-LUTIDINIUM PERCHLORATE (0.0987 M)

RUN 2-50

Varian A-60 NMR Spectrometer

Internal Standard: Ethylene carbonate (0.4003 M)

Time (10^5 sec)	Integration (τ 4.5)	Integration (Int. Std.)	(a - x)	Log (a - x)	$10^6 k_t$ (sec^{-1})
0	29.0	64.4	.02000	$\bar{2}.3010$	
2.745	13.5	44.6	.01336	$\bar{2}.1258$	1.47
4.320	20.0	81.0	.01090	$\bar{2}.0374$	1.41
6.048	12.0	65.0	.00838	$\bar{3}.9232$	1.48
7.236	12.0	73.0	.00727	$\bar{3}.8615$	1.60
9.729	9.4	80.0	.00520	$\bar{3}.7160$	1.39

$10^6 k_{av.} = 1.47 \pm 0.06$

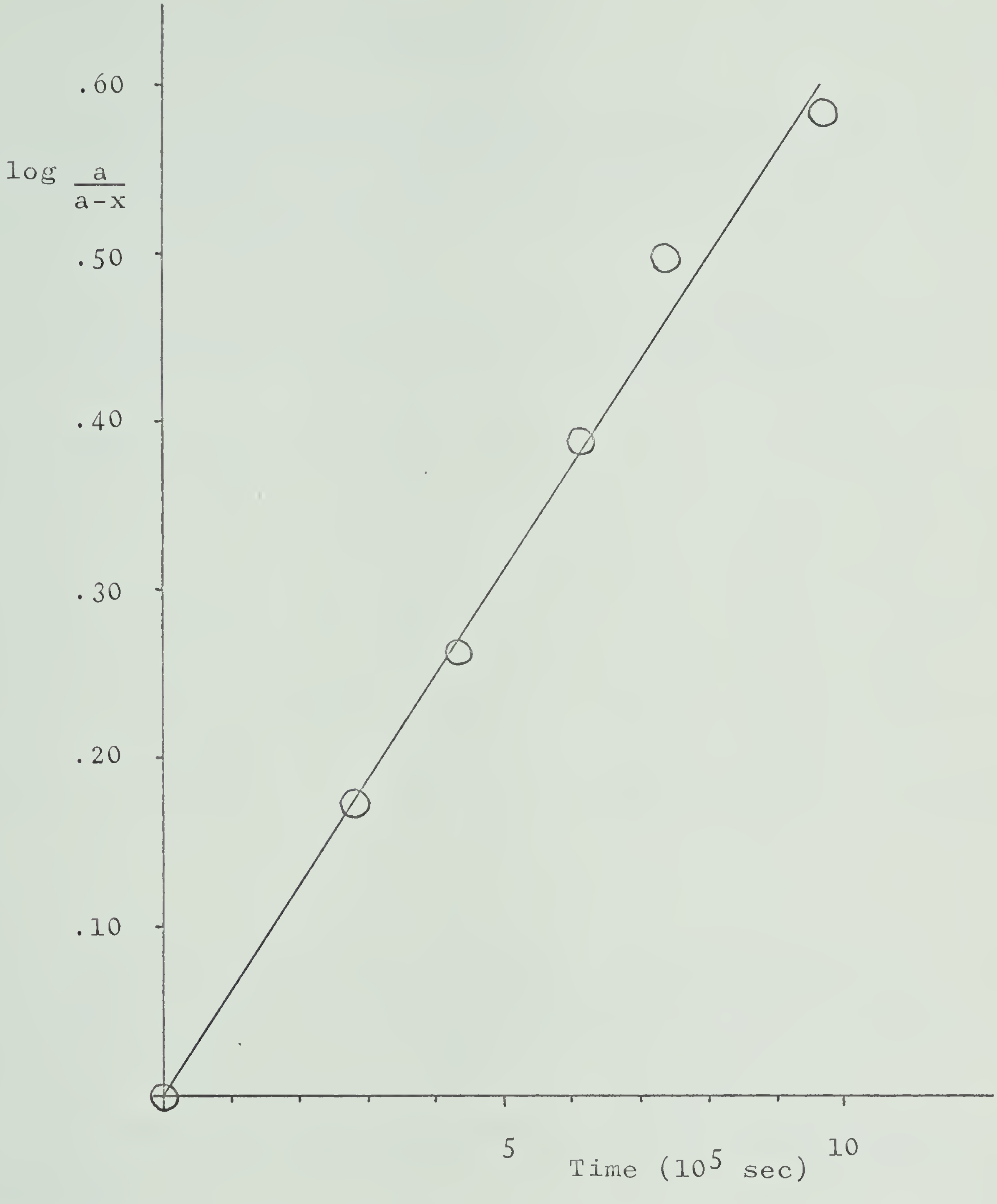


Figure VIII. Solvolysis of 0.0200 M phenacylethylmethylsulfonium perchlorate in anyhdrous methanol at 90.00° with added 2,6-lutidine (0.1013 M) and added 2,6-lutidinium perchlorate (0.0987 M) Run 2-50.

TABLE IV

SOLVOLYSIS OF PHENACYLETHYLMETHYLSULFONIUM PERCHLORATE IN ANHYDROUS METHANOL (k_t OBTAINED FROM INITIAL SLOPE OF THE LOG (a - x) VS TIME PLOT)

Run	Temperature	[Sulfonium Salt]	[Lutidine]	Method	$10^7 k_t$ (sec^{-1})
1-105	90.00	0.02		Tit.	8.6
1-167	90.00	0.02		Tit.	9.1
1-208	70.00	0.02		Tit.	0.92
1-292	90.00	0.02		n.m.r.	9.0
2-11	90.00	0.02	0.06	n.m.r.	77
2-50*	90.00	0.02	0.10	n.m.r.	14.7±0.6

* The reaction medium also contains 2,6-lutidinium perchlorate (0.10 M). The rate constant was not obtained in the same manner as the others; it was calculated as an average ofthe rate constants obtained from the following equation:

$$k_t = \frac{2.303}{t} \log \frac{a}{a - x}$$

RACEMIZATION STUDIES

The racemization rates were studied by measuring the change of rotation with time. The data are summarized in Table VII. Incident light of different wavelengths was employed for different runs. Using shorter wavelengths increases the optical rotation (Figure IV), thus permitting greater precision in rate determinations. The first-order rate constants were calculated from the relationship:

$$k = \frac{2.303}{t} \log \frac{\alpha_\infty - \alpha_0}{\alpha_\infty - \alpha_t}$$

where α_∞ is the optical rotation measured after ten half-lives of racemization (0.000±0.002) and α_t is the rotation at time t. Reactions were usually followed to ca. 80 per cent completion and good straight lines were obtained when log $(\alpha_\infty - \alpha_t)$ was plotted vs time. A typical example of a polarimetric rate analysis, Run 1-249, is shown in Table VI, with the corresponding plot of log $(\alpha_\infty - \alpha_t)$ illustrated in Figure IX.

The rate constant, k_1, the specific first-order rate constant for the conversion of one enantiomer to the other as illustrated in the scheme below

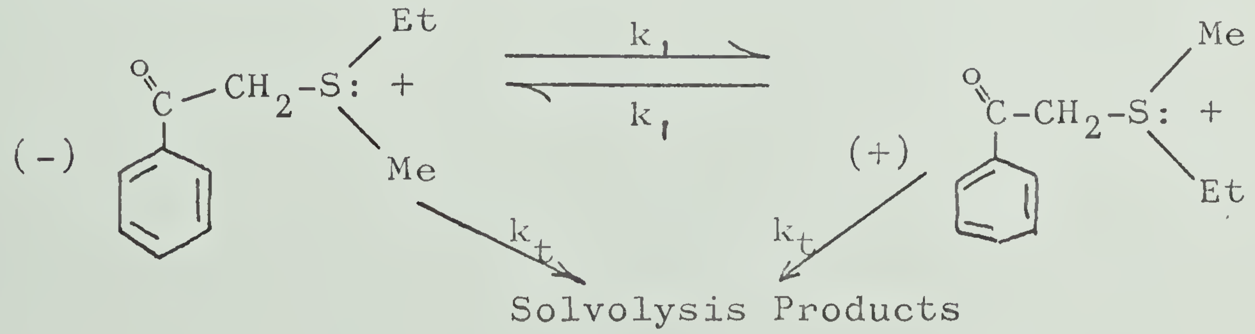


TABLE VI

RACEMIZATION OF 0.0200 M (-)-PHENACYLETHYLMETHYLSULFONIUM PERCHLORATE IN ANHYDROUS METHANOL AT 50.00° WITH ADDED PERCHLORIC ACID (2.99×10^{-3} M) RUN 1-249

Time (10^4 sec)	α^{25}_{365}	log $(\alpha_\infty - \alpha_t)$	$10^6 k_\alpha$ (sec^{-1})
0	-0.245	$\bar{1}.389$	——
6.12	-0.193	$\bar{1}.286$	3.89
8.82	-0.176	$\bar{1}.246$	3.75
14.76	-0.141	$\bar{1}.149$	3.75
18.36	-0.123	$\bar{1}.090$	3.75
24.12	-0.102	$\bar{1}.009$	3.63
27.90	-0.088	$\bar{2}.944$	3.67
32.04	-0.074	$\bar{2}.869$	3.74
36.72	-0.064	$\bar{2}.806$	3.66
250.56	0.000		

Average 3.73 ± 0.06

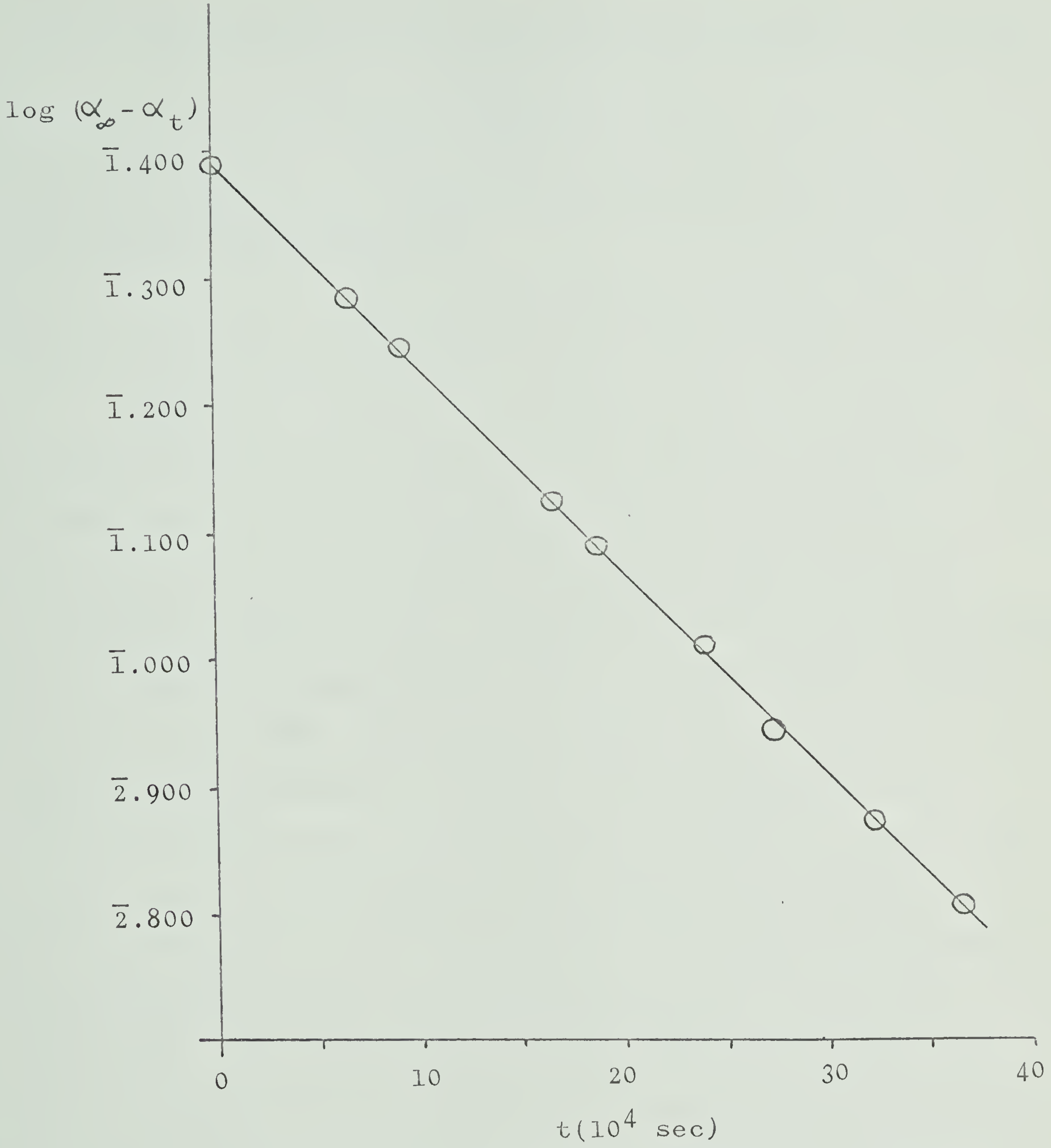


Figure IX. Racemization of .0200 M (-)-phenacylethylmethylsulfonium perchlorate @ 50°C in anhydrous methanol in the presence of perchloric acid (2.99×10^{-3} M) Run I-249

can be calculated from the observed rate constants as follows:

$$k_{rac.} = 2k_1 = k_\alpha - k_t$$

Since k_t is so small compared to k_α ($k_\alpha = 600\ k_t$), then to an excellent approximation:

$$k_{rac.} = 2k_1 = k_\alpha$$

The values of k_1 are also presented in Table VII.

There are a number of noteworthy features in Table VII. It may be noted that the polarity of the solvent has only a small effect on the racemization rate. Changing the solvent from acetone (Dielectric constant 21.2) to methanol (Dielectric constant 33.6) results in only a 17 per cent increase in the rate of racemization (Runs 1-95 and 1-245). It may also be noted that the presence of base in the reaction medium causes a marked increase in the racemization rate. Even the small amount of base (0.0007 M) present in Run 1-239 causes a 4.3 fold increase in the rate of racemization. As the base concentration increases the rate increases and then levels off at higher base concentrations (Cf. Runs 1-147 and 2-53). From Run 1-259 it is seen that the presence of even a weak base such as 2,6-lutidine results in a large increase in the reaction rate. This behaviour in basic solution is again associated with ylide formation.

Since the method used for the preparation of anhydrous methanol (12) may result in a trace of base being present in the form of ammonia, Runs 1-237, 1-243, 1-245, 1-247 and 1-249

were studied with added acid. The acid neutralizes any trace quantities of base and ensures that no ylide is formed. Ultraviolet spectra of the sulfonium salt in methanol with various concentrations of acid indicate that the presence of 0.003 M perchloric acid in the above runs is sufficient to ensure that no ylide is formed (Experimental section).

Experiments were performed to ensure that the excess loss of optical activity was due to racemization and not decomposition of the substrate. A methanolic solution of (-)-phenacylethylmethylsulfonium perchlorate was maintained at 70° for ten half-lives of racemization. The crystals isolated from the reaction mixture had melting point, n.m.r. and infrared spectra identical with those of the racemic salt (Laboratory notebook ref. 1-256). The ultraviolet spectra of a freshly prepared solution of the sulfonium perchlorate in neutral and basic solutions were taken. In the basic medium sufficient base, a 2-fold excess, was added to completely convert the salt to the ylide. After 5 half-lives of racemization the spectra were again taken in the same manner as above. Within experimental error the corresponding initial and final spectra and extinction coefficients were identical, indicating that no decomposition of the substrate had occurred (Laboratory notebook ref. 1-218). Details of these experiments are given in the Experimental section.

The racemization rate was also measured in the presence

of 0.097 M ethyl methyl sulfide (Run 1-247). The racemization rates were the same, within experimental error, in the presence and absence of sulfide.

TABLE VII. THE RACEMIZATION OF PHENACYLETHYLMETHYLSULFONIUM PERCHLORATE UNDER VARIOUS CONDITIONS

Run	Isomer	[I]	[NaOMe]	[$HClO_4$]	Solvent	Temp.	λ (mμ)	$10^5 k_\alpha$ (sec^{-1})	$10^5 k_1$ (sec^{-1})
1-95	(-)	.020	—	—	Acetone	70	589	4.76 ± 0.02	2.38 ± 0.01
1-231	(-)	.020	—	—	Methanol	70	436	7.60 ± 0.29	3.80 ± 0.15
1-124	(-)	.020	—	—	Methanol	90	589	67.6 ± 1.9	33.8 ± 1.0
1-237[a]	(-)	.020	—	—	Methanol	70	365	5.78 ± 0.12	2.89 ± 0.06
1-243	(-)	.020	—	0.10	Methanol	70	365	5.60 ± 0.14	2.80 ± 0.07
1-245	(-)	.020	—	0.003	Methanol	70	365	5.58 ± 0.18	2.79 ± 0.09
1-249	(-)	.020	—	0.003	Methanol	50	365	.373 ± .006	.186 ± .003
1-247[b]	(-)	.020	—	0.003	Methanol	70	365	5.58 ± 0.11	2.79 ± 0.06
1-259[c]	(-)	.020	—	—	Methanol	70	365	46.9 ± 1.3	23.4 ± 0.7
1-239	(-)	.020	.0007	—	Methanol	70	365	30.9 ± 1.4	15.4 ± 0.7
1-157	(-)	.030	.030	—	Methanol	50	589	59.2 ± 0.7	29.6 ± 0.4
1-147	(-)	.030	.090	—	Methanol	50	589	75.0 ± 1.7	37.5 ± 0.9
1-151	(-)	.030	.030	—	Methanol	25	589	2.81 ± 0.07	1.40 ± 0.04
2-53	(-)	.030	.21	—	Methanol	50	436	71.6 ± 1.8	35.8 ± 0.9

a) Contains 5 ml. of glacial acetic acid in 100 ml. of solution

b) Solution is 0.097 M in ethyl methyl sulfide

c) Solution is 0.036 M in 2,6-lutidine

PRODUCT ANALYSES

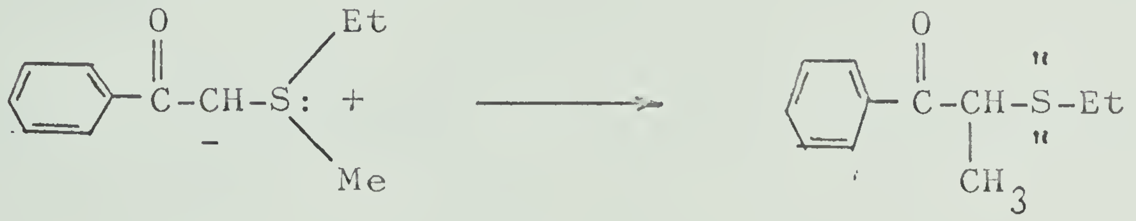
The solvolysis of phenacylethylmethylsulfonium perchlorate produces several products. Analyses by gas chromatography indicate the formation of at least ten products (many of these in trace amounts only); thin layer chromatography indicates upwards of twenty products. Only the major products were analyzed. Isolation of products was accomplished by preparative thin layer chromatography, and structures assigned by comparing the n.m.r., infrared and mass spectra of the isolated products with those of authentic samples. A comparison of retention times on gas chromatography of the isolated and authentic samples was also made.

For quantitative analyses by gas chromatography, the solvolysis products were concentrated and a known amount of an internal standard added. The area of each component peak relative to the peak area of the internal standard was calculated. This information was used in conjunction with a set of calibration curves to obtain the amount of each component present in the solution. A detailed account of this method is given in the Experimental section.

The major products of methanolysis of phenacylethylmethylsulfonium perchlorate are 2-methylthioacetophenone and 2-ethylthioacetophenone, produced in the amounts of 47 and 18 mole per cent respectively. Other products were produced in much smaller amounts and quantitative analyses were not made for them.

With a three fold molar excess of 2,6-lutidine present during the solvolysis the major products produced were 2-methylthioacetophenone, 2-ethylthioacetophenone, methyl benzoate and acetophenone. These were produced in the amounts of 11, 8, 20, and 11 mole per cent respectively.

It was considered possible that 2-ethylthiopropiophenone could be formed under our solvolysis conditions, as a result of a Stevens rearrangement (13):

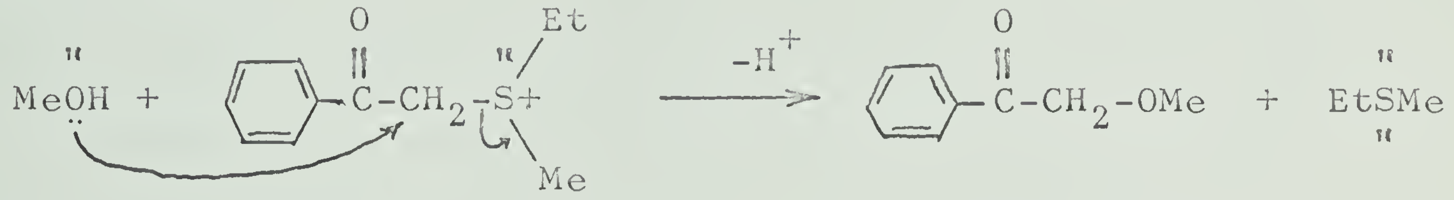


This material was synthesized and shown to be stable for at least six days in refluxing methanol containing sodium methoxide. It was also shown to be stable under the conditions used for analyses by gas chromatography. Studies on the reaction solution by n.m.r. spectroscopy and gas chromatography clearly showed that 2-ethylthiopropiophenone is not produced in the solvolysis reactions in the presence or absence of added 2,6-lutidine.

α-Ethylthiomethoxystyrene is formed by refluxing ethylmethylsulfonium phenacylide in water for $4\frac{1}{2}$ hours. Ratts and Yao (14) report the formation of similar products when they allowed aqueous or methanolic solutions of various ylides to reflux for several hours. Conceivably , α-ethylthiomethoxystyrene was formed under our reaction conditions; this

material was also synthesized. It was shown to be stable under the conditions used for analyses by gas chromatography. Studies on the reaction solution by n.m.r. spectroscopy and gas chromatography showed that α-ethylthiomethoxystyrene is not produced in the solvolysis reactions in the presence or absence of 2,6-lutidine.

Ethyl methyl sulfide was considered a possible product from our solvolysis reaction by a reaction such as the following:



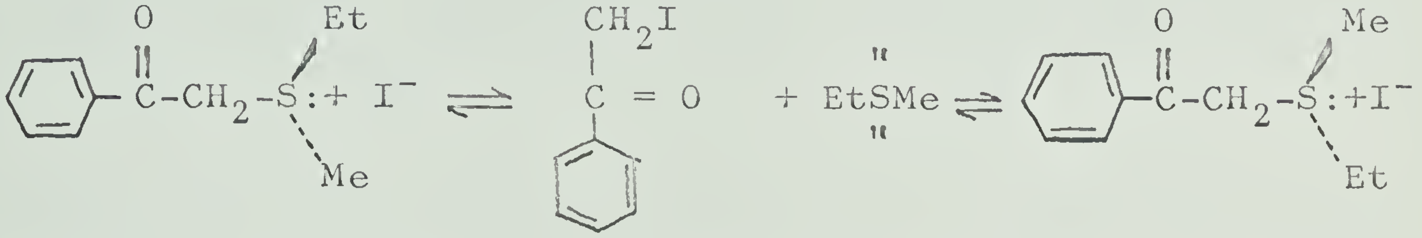
An analysis by gas chromatography indicated that the solvolysis reaction produces at most 1 per cent of ethyl methyl sulfide.

DISCUSSION

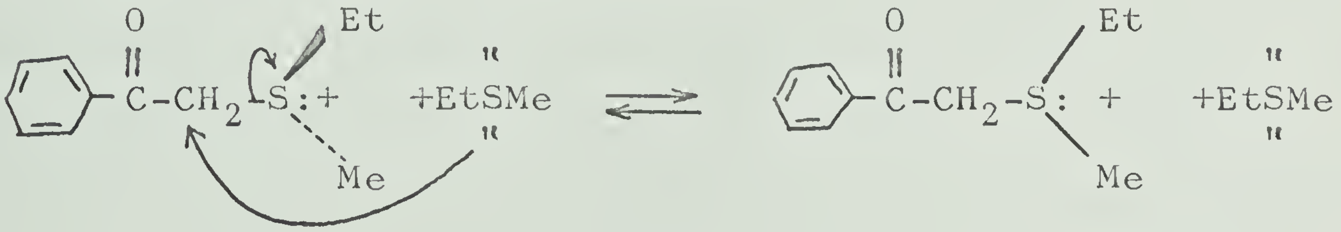
Phenacylethylmethylsulfonium perchlorate racemizes 600 times faster than it solvolyzes in methanol at 70°.

Racemic starting material was recovered in 88 per cent yield when optically active sulfonium salt was allowed to react in methanol for 10 half-lives of racemization. A more quantitative result was obtained by an ultraviolet analysis in which it was shown that no loss of absorbance of the starting material was found after 5 half-lives of racemization. Therefore the loss of optical activity is due to racemization of the sulfonium salt and does not result from its decomposition.

A number of mechanisms could conceivably account for the racemization of the sulfonium salt. It was shown by Kenyon et al (8) that racemization of the sulfonium iodide involved a displacement of ethyl methyl sulfide by a reversible nucleophilic attack on carbon by the anion as shown below:

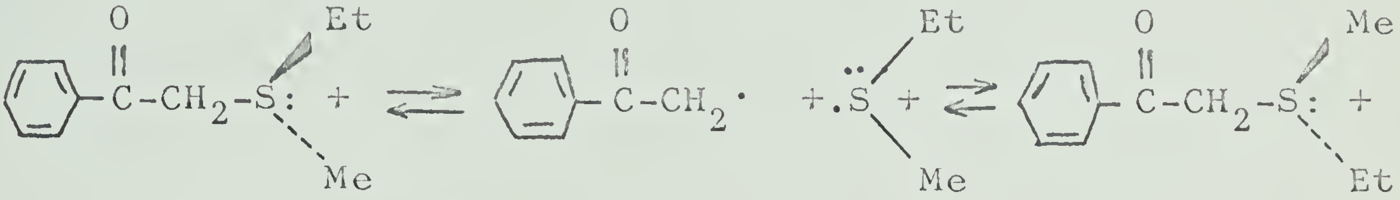


This cannot account for the excess racemization in sulfonium perchlorate salts because the perchlorate anion is non-nucleophilic and will not displace the sulfide group. Racemization could involve a displacement of ethyl methyl sulfide by another molecule of ethyl methyl sulfide generated by solvolysis of the sulfonium salt:



From Table VI it may be seen that the rates of racemization in the presence of a five molar excess of ethyl methyl sulfide and in its absence are identical within experimental error. Consequently this mechanism cannot account for the racemization. Heterolytic carbon-sulfur bond cleavage and recombination to yield racemic salt has been considered and rejected as a racemization mechanism for the t-butylethylmethylsulfonium

salts. Such a mechanism would be even more unfavourable for phenacylethylmethylsulfonium salts. An alternative scheme for racemization would be homolysis of the carbon-sulfur bond with subsequent recombination to yield racemic salt as shown below:



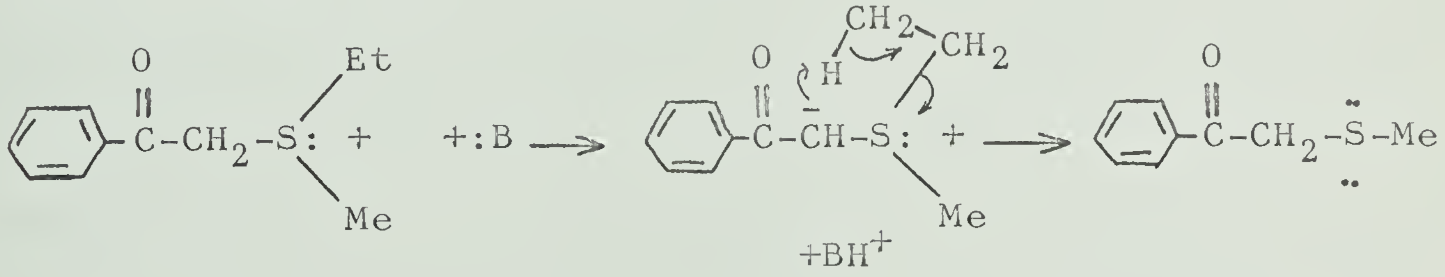
Pyramidal inversion about the central sulfur atom would also be a highly possible mechanism for racemization. Since this mechanism has been found to account for the major amount of racemization in other sulfonium salt systems (9-11), it may account for the racemization in this system as well.

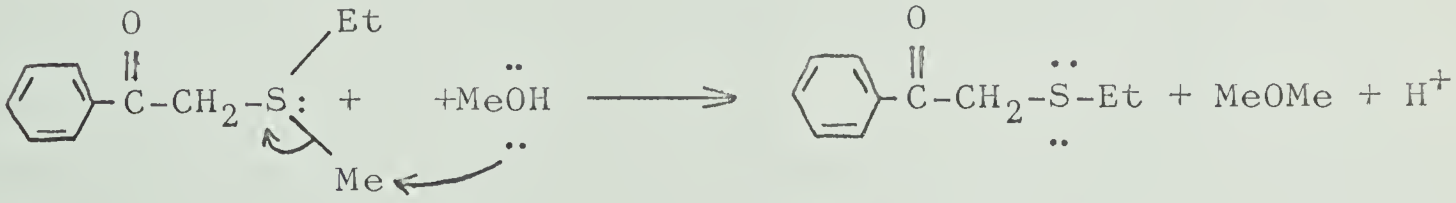
A distinction between these latter two mechanisms may be made by examining the decomposition products. If bond homolysis is to account for racemization, then products of free radical reactions should be observed. Acetophenone would be the most likely product to be formed from such a reaction. The decomposition reaction produces 2-methylthioacetophenone and 2-ethylthioacetophenone in 65 per cent yield. No trace of acetophenone is formed. Even if one assumed that all the rest of the decomposition products resulted completely from free radical reactions, only 35 per cent of the total products would have arisen from such reactions. Since racemization is 600 times faster than solvolysis, this assumption requires carbon-sulfur bond

heterolysis and recombination to occur 1800 times with only one of these cleavages resulting in free radical products. It should be borne in mind that 1800 is a minimum figure since it inherently assumes that all of the unidentified products have come from free radical reactions. Since the species resulting from carbon-sulfur bond homolysis would be highly reactive and not this selective, this mechanism cannot account for the racemization of phenacylethylmethylsulfonium perchlorate.

This leaves only one mechanism which can account for the racemization, pyramidal inversion about the sulfur center.

It is not clear how the decomposision products, 2-methylthioacetophenone and 2-ethylthioacetophenone, are formed, but their formation can be at least formally represented by the following equations:





The decomposition of the sulfonium salt in the presence of 2,6-lutidine was shown to result in the products 2-methylthioacetophenone, 2-ethylthioacetophenone, methyl benzoate

and acetophenone in the amounts of 11, 8, 20, and 11 mole per cent respectively. Comparing the decomposition of the sulfonium salt in the presence and absence of 2,6-lutidine, the difference in products and the large difference in the rates of decomposition, Table IV, clearly indicates that the two reactions follow different pathways for cleavage.

Benzylethylmethylsulfonium perchlorate and *p*-nitrobenzylethylmethylsulfonium perchlorate were found to racemize *ca*. twice as fast as phenacylethylmethylsulfonium perchlorate (11). It would be expected that the non-bonded interactions would be approximately the same for the benzyl systems and the phenacyl system, so that the difference in rates would not be due to steric effects. The difference may be due to the large difference in the inductive effects of the benzyl or *p*-nitrobenzyl and the phenacyl groups. However, such a small rate difference indicates that the inductive effect on the rate of racemization of sulfonium salts is very small, if present at all.

t-Butylethylmethylsulfonium and 1-substituted *t*-butylethylmethylsulfonium salts racemize much faster than phenacylethylmethylsulfonium salts (9). This is consistent with the *t*-butyl group being much larger than the phenacyl group and causing a steric acceleration of the rate.

ACTIVATION PARAMETERS

To determine the effect of temperature on the rates of solvolysis and racemization of phenacylethylmethylsulfonium perchlorate in methanol, the Arrhenius equation was used:

$$k = Ae^{-Ea/RT}$$

The heat of activation, $\Delta H^{\ddagger}$, for reactions in solution is given by (15):

$$\Delta H^{\ddagger} = Ea - RT$$

The entropy of activation, $\Delta S^{\ddagger}$, is obtained from the equation (15):

$$k = \kappa\, k_B T/h \quad x \quad e^{\Delta S^{\ddagger}/R} \; x \; e^{-\Delta H^{\ddagger}/RT}$$

where k_B is Boltzman's constant, h is Planck's constant and κ is the fraction of the transition state species which leads to products. For solvolysis, κ is assumed to be unity. For racemization, where k is k_1, the specific first-order rate constant for the conversion of one enantiomer to the other, the planar transition state should lead to one enantiomer as favourably as it leads to the other one. For this reason, κ is assumed to be 0.5 when calculating the entropy of activation for racemization. The entropy of activation, $\Delta S^{\ddagger}$, is therefore given by the following equation:

$$\Delta S^{\ddagger} = 4.576 \quad \log k - \log (2.083 \times 10^{10} \kappa\, T) + \frac{\Delta H^{\ddagger}}{4.576 \times 10^{-3} T} \quad \text{e.u.}$$

The values calculated for the enthalpy and entropy of activation for the racemization and solvolysis of phenacylethylmethylsulfonium perchlorate at 70° in methanol are as follows:

Solvolysis: $\Delta H^{\ddagger} = 27.\pm 3$ kcal/mole

$\Delta S^{\ddagger} = -11\pm 11$ e.u.

Racemization : $\Delta H^{\ddagger} = 29.0\pm .5$ kcal/mole

$\Delta S^{\ddagger} = 4.4\pm .6$ e.u.

The errors in the rate constants for the solvolysis of the sulfonium salt are very large. Hence, the activation parameters for the solvolysis reaction are at best only approximations.

EXPERIMENTAL

PHYSICAL MEASUREMENTS

All melting points were obtained using a Hershberg-type melting point apparatus and a set of Anschutz thermometers. All values are uncorrected.

Refractive indices were obtained on a Bausch and Lomb Abbe 3L Refractometer, maintained at a constant temperature by means of a water jacket attached to a constant temperature bath.

Nuclear magnetic resonance spectra were recorded on a Varian Analytical Spectrophotometer Model A-60.

Infrared spectra were recorded on a Perkin-Elmer Recording Infrared Spectrophotometer Model 421.

Ultraviolet and visible spectra were obtained using a Perkin-Elmer Ultraviolet-visible Spectrophotometer Model 202. A Beckman DU Spectrophotometer Model 2400 was employed where precise absorbance values were required.

Optical rotation measurements were obtained on a Perkin-Elmer Polarimeter Model 141.

Gas chromatographic analyses were made on a Varian Aerograph Model A 90-P3.

Elemental analyses were performed by Mrs. D. Mahlow and Mrs. A. Dunn.

SOLVENTS

Anhydrous methanol

Anhydrous methanol was prepared by Lund and Bjerrum's method from commercially available reagent methanol (max. water 0.02%) by treatment with magnesium methoxide as described by Fieser (12), b.p. 63° at 705 mm. A Karl Fischer titration (16) was performed and showed that the solvent contained less than 0.001 per cent water.

Anhydrous acetone

Drierite (non-indicating, 1 lb.) was placed in a clean, dry flask and 1 liter of Shawinigan Reagent Grade acetone added. The flask was stoppered and the contents shaken occasionally for 4 hours. The pure, dry acetone was fractionally distilled, discarding the first 200 ml. of distillate, b.p. 55° at 710 mm. The water content of the acetone was determined by Karl Fischer titration using anhydrous pyridine as the solvent as suggested by Smith, Fainberg and Winstein (17). The solvent was found to contain 0.01 per cent water.

Anhydrous pyridine

Eastman Karl Fischer Grade pyridine was stored over potassium hydroxide in a dark bottle.

REAGENTS AND MATERIALS

2,6-Lutidine

Eastman Practical Grade 2,6-lutidine was dried over potassium hydroxide for several days, followed by refluxing over and distillation from barium oxide as described by Fieser for the preparation of anhydrous pyridine (19). The center cut from this distillation was treated with boron trifluoride as described by Brown *et al* (20). Pure 2,6-lutidine was then fractionally distilled from this mixture (b.p. 139-141 at 705 mm.). n_D^{25} 1.4954 (reported (20): b.p. 143 at 760 mm., n_D^{25} 1.4953).

Standard sodium methoxide solution for titrations

A weighed amount of freshly cleaned sodium was added to one gallon of Shawinigan Reagent Grade methanol. The resulting solution was standardized with Fisher Certified Primary Standard potassium hydrogen phthalate in water using phenolphthalein as indicator. Restandardization showed the solution to be stable for at least two years when it is stored in a tightly-stoppered dark bottle.

Ethyl methyl sulfide

Eastman Kodak ethyl methyl sulfide was used directly without further purification.

Phenacyl bromide

Eastman Kodak phenacyl bromide was used directly without further purification.

Phenacylethylmethylsulfonium bromide

Phenacylethylmethylsulfonium bromide was prepared in a manner similar to that used by Smiles (7) by dissolving phenacyl bromide (23.1 gm., 0.116 moles) in 50 ml. of acetone and adding this to ethyl methyl sulfide (8.8 gm., 0.116 moles). This mixture was allowed to stand in the dark at room temperature for 2½ hours. A large excess of ether was added to the acetone solution, and this mixture placed in the freezer for two days. The resulting crystals were filtered, washed with ether, and recrystallized from methanol-ether to yield 23.2 gm. (73%) of pure phenacylethylmethylsulfonium bromide. M.p. 89-90 (dec.). N.m.r. ($CDCl_3$): (τ) 2.4 (m, 5H); 3.80 (s,d,2H), 6.15 (q,d,J = 7.5 cps, 2H), 6.78 (s, 3H), 8.60 (t, J = 7.5 cps, 3H). Infrared: 3060, 3005, 3000-2800 (several), 1678, 1665, 1590, 1575, 1210, 755, and 680 cm^{-1}.

Anal. Calcd for $C_{11}H_{15}OBrS$: C, 48.01; H,5.41

Found: C,47.83, 47.53; H, 5.76; 5.91

(-)-2R,3R-Dibenzoyltartaric acid monohydrate

From 200 gm. (1.3 moles) of (+)-2R,3R-tartaric acid was obtained 385 gm. (78 per cent) of (-)-2R,3R-dibenzoyltartaric acid monohydrate, using the method described by Butler (18). M.P. 83-85° (reported (18): 88-89°). $[\alpha]_D^{25}$ -114.3 (c = 0.28, methanol); reported (18): -116.0; (21) -114.8. N.m.r. ($CDCl_3$): τ 4.07 (s, 2H), 2.6 (m,6H), 2.0 (m, 4H), 1.17 (s, 4H). Infrared : 3600-2500, 1740, 1608, 1590, 1495, 1458, 1250, 1110, 1095 and 710 cm^{-1}. Ultraviolet (ethanol): λ_{max} 230 mu (log ϵ 4.40).

Anal. Calcd for $C_{18}H_{16}O_9$: C, 57.45 ; H, 4.29

Found : C, 57.38, 57.12 ; H, 4.32, 4.18

(-)-Phenacylethylmethylsulfonium 2R,3R-dibenzoylhydrogentartarate

Phenacylethylmethylsulfonium bromide (31.55 gm., 0.115 moles) was dissolved in the minimum amount of methanol and passed through a Dowex 1-X8 anion exchange column in its hydroxide form, using methanol as the eluent. The effluent was received in a flask containing (-)-2R,3R-dibenzoyltartaric acid monohydrate (42.9 gm., 0.114 moles). When elution was complete (determined by testing the effluent for base using phenolphthalein as indicator), the solution was concentrated to 300 ml., filtered and placed in the freezer for one day. The resulting solution and crystals were separated, the crystals washed with ether and recrystallized from methanol to yield 12.75 gm. (20 per cent) of (-)-phenacylethylmethylsulfonium 2R,3R-dibenzoylhydrogentartarate. M.p. 138-138.5 (dec). $\left[\alpha\right]_D^{25}$ -88.2 (c=0.443, methanol). N.m.r. (dimethylsulfoxide-d_6): τ 2.35 (m, 17H), 4.36 (s, 2H), 6.63 (q, J = 7 cps, 3H), 7.10 (s, 3H), 8.69 (t, J = 7 cps, 3H). Infrared: 3060, 3030, 2960, 2905, 1710, 1590, 1450, 1265, 748 and 710 cm^{-1}.

Anal. Calcd. for $C_{29}H_{28}O_9S$: C, 63.03, H, 5.12, S, 5.80

Found: C, 63.16, 63.29; H, 5.39, 5.03; S, 5.66, 6.07.

(dl)-phenacylethylmethylsulfonium perchlorate

(dl)-phenacylethylmethylsulfonium bromide (23 gm., 0.084 moles) was dissolved in the minimum amount of methanol and passed through a Dowex 1-X8 anion exchange column in hydroxide

form, using methanol as the eluent. The effluent was received in a flask containing 11.2 gm. of 60 per cent perchloric acid (0.067 moles of $HClO_4$). When elution was complete (determined in the same manner as above), the solution was concentrated to 100 ml., filtered, ether added to the cloud point and the solution placed in the freezer overnight. The resulting crystals were recrystallized twice from acetone-ether and dried in vacuo over phosphorous pentoxide to yield 17.7 gm. (90 per cent) of pure (dl)-phenacylethylmethylsulfonium perchlorate. M.p. 143.5-145°. N.m.r. (dimethylsulfoxide-d_6): τ 2.15 (m, 5H), 4.56 (s, 2H), 6.56 (q, J = 7.5 cps, 2H), 7.03 (s, 3H), 8.57 (t, J = 7.5 cps, 3H). N.m.r. (CF_3COOH): τ 2.2 (m, 5H), 4.75 (s, 2H), 6.43 (m, 2H), 6.91 (s, 3H), 8.38 (t, J = 7.5 cps, 3H). Infrared: 3010, 2980, 2940, 1675, 1590, 1445, 1220, 1150-1050 (broad), 750 and 680 cm^{-1}.

(-)-Phenacylethylmethylsulfonium perchlorate

(-)-Phenacylethylmethylsulfonium 2R,3R-dibenzoylhydrogentartarate (13.5 gm., 0.025 moles) was dissolved in the minimum amount of methanol and passed through a Dowex 1-X8 anion exchange column in its hydroxide form, using methanol as the eluent. The effluent was received in a flask containing 3.75 gm. of 60 per cent perchloric acid (0.0225 moles of $HClO_4$). The remainder of the workup was carried out in a manner similar to that used for the (dl)-salt to yield 6.50 gm. (98 per cent) of pure (-)-phenacylethylmethylsulfonium perchlorate. M.P. 144-144.5°. $[\alpha]_D^{25}$ -10.8 (c=0.5, methanol). N.m.r. (dimethylsulfoxide-d_6): τ 2.2 (m, 5H), 4.50 (s, 2H), 6.59 (q, J = 7 cps, 2H), 7.06 (3, 3H), 8.59 (t, J = 7 cps, 3H), Infrared: 3010,

2980, 1670, 1590, 1440, 1210, 1110, 1100, 750 and 680 cm^{-1}.

Anal. Calcd. for $C_{11}H_{15}ClO_5S$: C, 44.82 ; H, 5.13

Found: C, 45.05, 44.95; H, 5.16, 5.40.

2-Methylthioacetophenone (Phenacyl methyl sulfide)

2-Methylthioacetophenone was prepared using Wahl's method (22). Freshly cleaned sodium (4.2 gm., 0.18 moles) was dissolved in absolute ethanol (200 ml.) and methanethiol (8.78gm., 0.18 moles), which had been cooled to -70°, was added to this solution. Phenacyl bromide (35.8 gm., 0.18 moles) was dissolved in the minimum amount of absolute ethanol and added to the above solution. The resulting mixture was allowed to gradually come to room temperature with stirring and then stirred for another 15 minutes. The sodium bromide was filtered off and the solution refluxed for 15 minutes. Solvent was removed on the rotary evaporator, water added to the residue and the mixture extracted with ether. The ether extract was washed with water, dried, the ether removed by distillation and the resulting oil distilled under vacuum to yield 12 gm. (40 per cent) of 2-methylthioacetophenone. B.p. 105° at 0.7 mm. (reported (23) b.p. 100-105° at 0.4 mm.), n_D^{25} 1.5820. N.m.r. (CCl_4): τ 2.10 (m, 2H), 2.55 (m, 3H), 6.40 (s, 2H), 7.97 (s, 3H), Infrared: 3100-3000 (several), 2980, 2920, 1670, 1595, 1445, 1270, 1015, 700, 680 and 640 cm^{-1}.

2-Ethylthioacetophenone (Phenacyl ethyl sulfide)

2-Ethylthioacetophenone was prepared according to the method described for the preparation of 2-methylthioaceto-

phenone. From sodium (3.60 gm., 0.157 moles), ethanethiol (9.72 gm., 0.157 moles) and phenacyl bromide (31.15 gm., 0.157 moles) was obtained 25 gm. (87 per cent yield) of 2-ethylthioacetophenone. B.p. 96° at 0.7 mm. $n_D^{25} = 1.5685$. N.m.r. (CCl_4): τ 2.15 (m, 2H), 2.7 (m, 3H), 6.42 (s, 2H), 7.53 (q, J = 7cps, 3H). Infrared: 3080, 3050, 2960, 2920, 2860, 1670, 1590, 1575, 1440, 1270, 1005, 715, 680 and 630 cm^{-1}.

2-Bromopropiophenone

2-Bromopropiophenone was prepared by the method of Higginbotham, Lapworth and Simpson (24) by adding bromine (15.6 gm., 0.098 moles) to a solution of propiophenone(13.1 gm., 0.098 moles) in 50 ml. of anhydrous ether at 0° with stirring. When addition of bromine was complete, the reaction mixture was allowed to come to room temperature, and stirring was continued for 1½ hours. The ether was removed by distillation through a 70 cm. Vigreux column, and the residue distilled under vacuum to yield 13.8 gm. (66 per cent) of pure 2-bromopropiophenone. B.p. 76-77° at 0.8 mm. (reported (24) b.p. 110-124° at 4 mm.) N.m.r. (CCl_4): τ 1.95 (m, 2H), 2.5 m, 3H), 4.75 (q, J = 6.5 cps, 1H), 8.18 (d, J = 6.5 cps, 3H).

2-Ethylthiopropiophenone

2-Ethylthiopropiophenone was prepared by the method described by Prelog _et al_ (25) by adding 2-bromopropiophenone (13.8 gm., 0.065 moles) to a solution of sodium ethyl mercaptide (0.065 moles) in absolute ethanol. When addition

was complete, the reaction mixture was refluxed for 7 hours and then allowed to stand overnight at room temperature. The sodium bromide was removed by filtration, most of the ethanol removed by distillation and water added to the residue. The aqueous mixture was ether extracted several times, and the combined ether extractions washed with water, dilute sodium hydroxide, water again and then dried. The ether was removed by distillation through a 70 cm. Vigreux column, and the residue vacuum distilled to yield 11 gm. (88 per cent) of pure 2-ethylthiopropiophenone. B.p. 100° at 1.0 mm. (reported (25) b.p. 100-102° at 0.3 mm.) N.m.r. (CCl_4):τ 1.95 (m, 2H), 2.50 (m, 3H), 5.73 (q, J = cps, 1H), 7.55 (m, 2H), 8.48 (d, J = 7 cps, 3H), 8.86 (t, J = 7.5 cps, 3H).

α-Ethylthiomethoxystyrene

α-Ethylthiomethoxystyrene was prepared by the method described by Ratts and Yao (14) by refluxing phenacylethylmethylsulfonium bromide (55.7 gm., 0.2 moles) in an aqueous solution of 5 per cent sodium hydroxide (165 ml., 0.2 moles) for 5 hours. The solution was cooled and extracted twice with ether. The combined ether extracts were washed with water, dried, the ether removed by distillation through a 70 cm. Vigreux column and the residue vacuum distilled. B.p. 82-84° at 0.7 mm. This product was found to be composed of two major components and one minor component by gas chromatography. These were separated by preparative gas chroma-

tography on a Carbowax 1500 column at 170°. The two major products were identified as 2-methylthioacetophenone and α-ethylthiomethoxystyrene, present in the mixture in ca. 40 per cent and 60 per cent respectively. The following spectral data is for α-ethylthiomethoxystyrene. N.m.r. (CCl_4): τ 2.65 (m, 5H), 5.05 (s, 2H), 5.31 (d, J = 3 cps, 1H), 5.83 (d, J = 3 cps, 1H), 7.31 (q, J = 7.5 cps, 2H), 8.68 (t, J = 7.5 cps, 1H). Infrared: 3080, 3060, 3030, 2970, 2920, 2870, 1687, 1595, 1445, 1270, 1260, 1110, 1010, 695 and 685 cm^{-1}.

Ethylene carbonate

Eastman Kodak Practical Grade ethylene carbonate was purified by fractional distillation in vacuo. B.p. 125-127° at 16.5 mm. (reported (26) b.p. 236° at 760 mm.) m.p. 39° (reported (26) m.p. 39°). N.m.r. ($CDCl_3$): τ 5.44 (s).

Racemization of (-)-phenacylethylmethylsulfonium perchlorate

Run 1-256

A solution of 0.295 gm. of (-)-phenacylethylmethylsulfonium perchlorate in 50 ml. of anhydrous methanol was prepared ($\alpha^{25}_{365} = -0.248 \pm 0.002$). This solution was placed in a constant temperature bath at 70.00 ± 0.02° for 27 hours (ten half-lives of racemization) at which time the rotation had decreased to $\alpha^{25}_{365} = 0.000 \pm 0.002$. Ether was added to this solution to the cloud point and the solution placed in the freezer for one day. The resulting white crystals were filtered, washed with ether and dried in vacuo over phosphorous pentoxide, yielding 0.259 gm. (88%) of phenacylethylmethylsulfonium perchlorate. The melting point (143.5-145°), as well as n.m.r. and infrared spectra indicated that the recovered material was racemic phenacylethylmethylsulfonium perchlorate.

Racemization of (-)-phenacylethylmethylsulfonium perchlorate

Run 1-218

A solution of 0.8843 gm. of (-)-phenacylethylmethylsulfonium perchlorate in 100 ml. of anhydrous methanol was prepared. A 1 ml. portion of this solution was diluted to 250 ml. and an ultraviolet spectrum using anhydrous methanol as a blank was obtained ($\log \epsilon = 4.10$, $\lambda = 250$ mu). Another 1 ml. portion of the initial solution was diluted to 250 ml. with anhydrous methanol and sodium methoxide, such that the

resulting solution was 10^{-2} M in sodium methoxide. An ultraviolet spectrum of this solution was obtained using 10^{-2} M sodium methoxide in anhydrous methanol as a blank (log ϵ = 4.03, λ= 297 mu). The remaining portion of the solution was maintained at 70.00 ± .02° for 5 half-lives of racemization. At this time ultraviolet spectra were again taken, using the procedures described above (log ϵ = 4.10, λ= 250 mu; log ϵ = 4.03, λ= 297 mu).

KINETICS

TITRIMETRIC RATES

The sulfonium salt was accurately weighed in a tared volumetric flask, and approximately half the required amount of solvent added. The flask was shaken vigourously until all the salt was dissolved (ca. 15 minutes), and the solution was diluted to the mark. The solution was equilibrated by shaking the flask 50 times.

Aliquots of this solution (5.5 ml.) were transferred to partially drawn out test tubes (15 x 125 mm.) which had been previously soaked overnight in a hot soap solution, rinsed eight times with distilled water, and then dried overnight in an oven at 120°. The test tubes were sealed and placed in a constant temperature oil bath; 90.00 ± 0.02 or 70.00 ± 0.02° C. At appropriate intervals of time the ampoules were withdrawn from the bath and shaken vigourously in an ice-methanol bath for 30 seconds in order to quench the

reaction. The first point was taken at least 5 minutes after the ampoules had been placed in the bath in order to ensure temperature equilibration. Infinity measurements on the reactions at 90° were taken after 10 half-lives of solvolysis.

The ampoules were allowed to equilibrate to 25° in a constant temperature bath for 5 minutes before being opened. Using a calibrated automatic pipette a 5 ml. aliquot was removed and delivered into a 50 ml. Erlenmeyer flask containing 25 ml. of absolute ethanol. Each sample was titrated for acid with a standard solution of sodium methoxide in methanol using bromphenol blue as the indicator. This particular indicator was chosen so as to have the end point in the acidic region. Above pH 7 it was found that one not only titrated the acid which had been produced, but the sulfonium salt as well.

RATES STUDIED BY NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

A standard solution of the racemic sulfonium salt was prepared, containing a standard amount of 2,6-lutidine and/or 2,6-lutidinium perchlorate if required. The solution was transferred in *ca*. 21 ml. aliquots to ampoules, the ampoules sealed, and placed in a constant temperature oil bath as described for the titrimetric rate analyses.

Reactions were quenched in an ice-methanol bath as described above, equilibrated to 25°, opened, and a 20 ml. aliquot transferred to a round-bottom flask by means of a calibrated automatic pipette. If the reaction mixture did

not contain 2,6-lutidine, a 5 ml. aliquot of 0.08 M 2,6-lutidine in methanol was added at this time. Solvent was removed on a rotary evaporator and the residue dissolved in 1 ml. of 0.40 M ethylene carbonate in dimethylsulfoxide-$\underline{d}_6$. A nuclear magnetic resonance spectrum was then obtained of this solution.

The integration of the n.m.r. signals corresponding to starting material (τ 4.56, 7.03 and 8.57) were measured and the amount of starting material still remaining was calculated relative to the internal standard, ethylene carbonate.

Infinity measurements were taken after 10 half-lives of solvolysis. The rate constants were obtained from the relationship:

$$k_t = \frac{2.303}{t} \log \frac{a}{a - x}$$

where a is the initial concentration of starting material and (a - x) is the concentration at time t.

POLARIMETRIC RATES

A standard solution of the optically active sulfonium salt was prepared and aliquots of it transferred to ampoules. The ampoules were sealed and placed in a constant temperature bath as described for the titrimetric rate analyses. Reactions were quenched in an ice-methanol bath as described previously, equilibrated to 25°, opened and an aliquot of the solution transferred to a 1 dm. polarimeter tube surrounded by a jacket through which water from a constant temperature bath

at 25° was circulated. The optical rotation was obtained from the digital readout of a Perkin-Elmer Polarimeter Model 141. "Zero" readings were obtained before and after each measurement. Rate constants were calculated on the basis of the experimental infinity obtained after 10 half-lives of racemization (0.000 ± 0.002).

METHANOLYSIS OF PHENACYLETHYLMETHYLSULFONIUM PERCHLORATE-CONTROL ANALYSES-RUN 2-35

A stock solution, 2-35-1, containing 2-methylthioacetophenone (0.115 M) and 2-ethylthioacetophenone (0.158 M) in carbon tetrachloride was prepared. Another standard solution, 2-35-2, containing ethyl phthalate (0.081 M) in carbon tetrachloride was also prepared.

A series of standard solutions containing various concentrations of the two components, 2-methylthioacetophenone and 2-ethylthioacetophenone, was prepared by a series of dilutions of the stock solution, 2-35-1, with solvent as shown in Table VIII.

TABLE VIII

STANDARD SOLUTIONS FOR THE PRODUCT ANALYSIS OF THE METHANOLYSIS OF PHENACYLETHYLMETHYLSULFONIUM PERCHLORATE

Solution	Aliquots of stock solution and solvent	
	2-35-1	Solvent
2-35-100	1 x 4.934	———
2-35-80	4 x 4.934	1 x 4.934
2-35-67	2 x 4.934	1 x 4.934
2-35-50	1 x 4.934	1 x 4.934
2-35-40	2 x 4.934	3 x 4.934
2-35-33	1 x 4.934	2 x 4.934
2-35-20	1 x 4.934	4 x 4.934
2-35-10*		

* Prepared by diluting 4.934 ml. of 2-35-20 with 4.934 ml. of solvent.

Control solutions were prepared by transferring a 4.934 ml. aliquot of each of these standard solutions to flasks containing a 4.934 ml. aliquot of 2-35-2, the standard solution of ethyl phthalate. The control solutions and the molarity of the components are given in Table IX.

TABLE IX

CONTROL SOLUTIONS FOR THE PRODUCT ANALYSIS OF THE METHANOLYSIS OF PHENACYLETHYLMETHYLSULFONIUM PERCHLORATE

Control	Molarity of Components[1]	
	2-Methylthioacetophenone	2-Ethylthioacetophenone
2-35-100-1	0.0575	0.0790
2-35-80-1	0.0460	0.0632
2-35-67-1	0.0383	0.0527
2-35-50-1	0.0288	0.0395
2-35-40-1	0.0230	0.0316
2-35-33-1	0.0192	0.0263
2-35-20-1	0.0115	0.0158
2-35-10-1	0.0058	0.0079

1) The molarity of ethyl phthalate, the internal standard, is 0.0405 in each control solution.

A 50 μl sample of each control solution was injected into the gas chromatographic apparatus. A 20 per cent silicone oil SE 30 on 60-80 mesh Chromosorb W column (6' x $\frac{1}{4}$")

was employed, using a helium flow rate of 60 cc/minute and a column temperature of 160°.

Peak areas were calculated using the formula:

$$A = h \times w_{\frac{1}{2}}$$

where h is the peak height and $w_{\frac{1}{2}}$ is the peak width at half height. Duplicates were made of each run. The area of each component relative to the area of the internal standard, ethyl phthalate, was calculated (data presented in Table X) and a calibration curve constructed by plotting the relative areas of each component vs the molarity of each component. A good straight line was obtained as illustrated in Figure X.

TABLE X

CONTROL ANALYSES OF THE PRODUCTS OF METHANOLYSIS OF PHENACYLETHYLMETHYLSULFONIUM PERCHLORATE

Control	$[A]^1$	Rel. Area A	$[B]^2$	Rel. Area B
2-35-100-1	0.0575	1.132	0.0790	
2-35-80-1	0.0460	0.834	0.0632	
2-35-67-1	0.0383	0.762	0.0527	1.060
2-35-50-1	0.0288	0.534	0.0395	0.777
2-35-40-1	0.0230	0.429	0.0316	0.621
2-35-33-1	0.0192	0.354	0.0263	0.514
2-35-20-1	0.0115	0.200	0.0158	0.294
2-35-10-1	0.0058	0.099	0.0079	0.148

1) A = 2-methylthioacetophenone 2) B = 2-ethylthioacetophenone

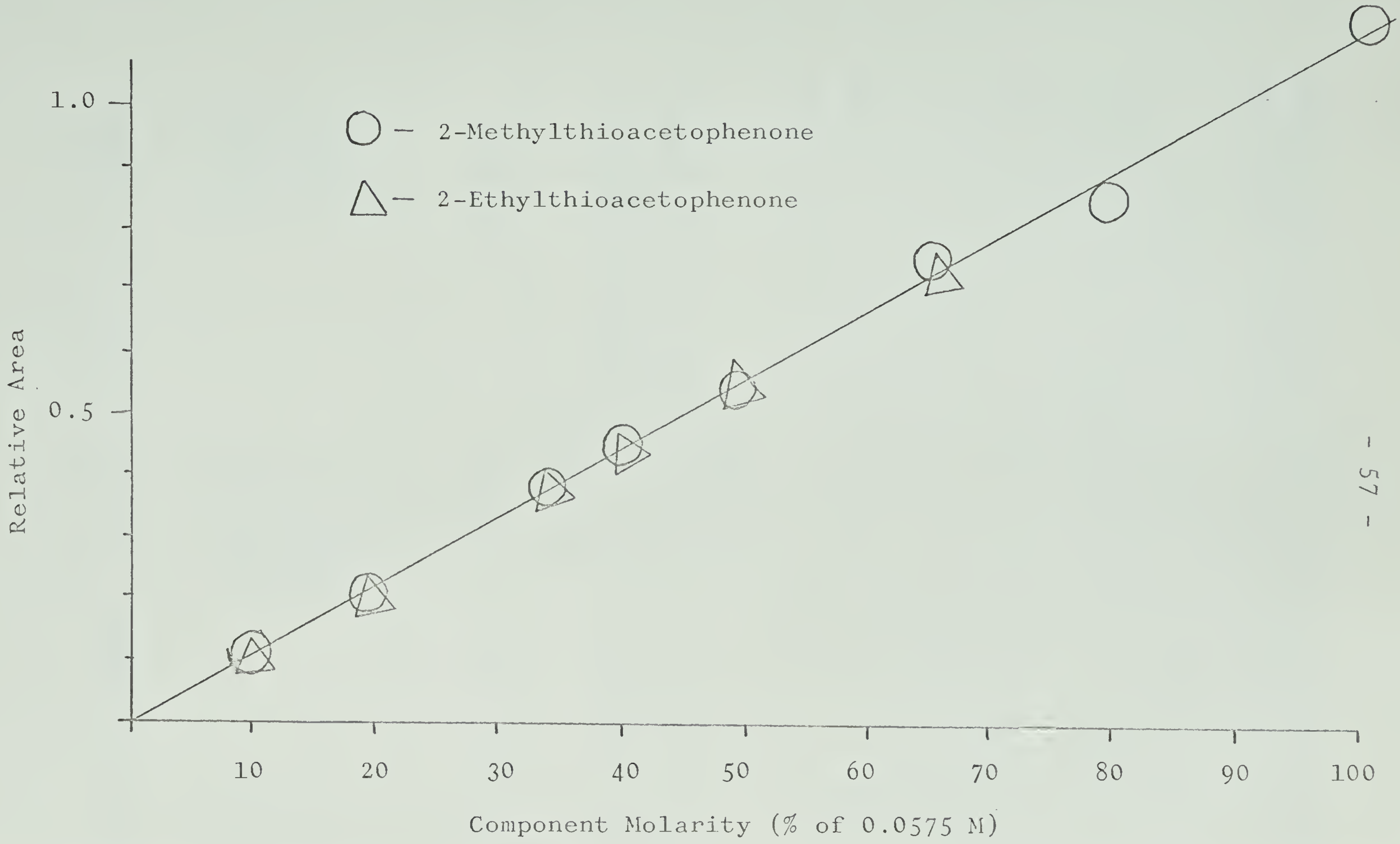


Figure X. Calibration curve for the product analysis of phenacylethylmethylsulfonium perchlorate in anhydrous methanol, using ethyl phthalate as internal standard. Run 2-35.

METHANOLYSIS OF PHENACYLETHYLMETHYLSULFONIUM PERCHLORATE WITH ADDED 2,6-LUTIDINE - CONTROL ANALYSES - RUN 2-19.

A stock solution, 2-19-1, containing methyl benzoate (0.150 M) and acetophenone (0.150 M) in carbon tetrachloride was prepared. A second stock solution, 2-19-2, containing ethyl phthalate in carbon tetrachloride was also prepared. A series of standard solutions containing various concentrations of the two components, methyl benzoate and acetophenone, was prepared by making a series of dilutions of the stock solution, 2-19-1, with solvent as shown in Table XI.

TABLE XI

STANDARD SOLUTIONS FOR THE PRODUCT ANALYSIS OF METHANOLYSIS OF PHENACYLETHYLMETHYLSULFONIUM PERCHLORATE WITH ADDED 2,6-LUTIDINE

Solution	Aliquots of Stock Solution & Solvent	
	2-19-1	Solvent
2-19-80	4 x 5.002	1 x 5.002
2-19-67	2 x 5.002	1 x 5.002
2-19-50	1 x 5.002	1 x 5.002
2.19-33	1 x 5.002	2 x 5.002
2-19-20	1 x 5.002	4 x 5.002
2-19-10*		

* Prepared by adding a 5.002 ml. aliquot of 2-19-20 to a 5.002 ml. aliquot of the solvent.

Control solutions were prepared by transferring a 5.002 ml. aliquot of each of these solutions to flasks containing a 5.002 ml. aliquot of 2-19-2, the standard solution of the internal standard, ethyl phthalate. The control solutions and the molarity of the components are listed in Table XII.

TABLE XII

CONTROL SOLUTIONS FOR THE PRODUCT ANALYSIS OF METHANOLYSIS OF PHENACYLETHYLMETHYLSULFONIUM PERCHLORATE WITH ADDED 2,6-LUTIDINE

Control	Molarity of Components	
	Methyl Benzoate or Acetophenone	Ethyl Phthalate
2-19-80-1	0.060	0.040
2-19-67-1	0.050	0.040
2-19-50-1	0.038	0.040
2-19-33-1	0.025	0.040
2-19-20-1	0.015	0.040
2-19-10-1	0.0075	0.040

A 50 μl sample of each control solution was injected into the gas chromatographic apparatus. A 20 per cent silicone oil SE 30 on 60-80 mesh Chromosorb W column (6' x $\frac{1}{4}$") was employed, using a helium flow rate of 60 cc/minute. The column was maintained at a temperature of 105° for 12 min. after each injection and then programmed at a rate of 30°

per minute to a temperature of 170°.

Peak areas were calculated using the formula:

$$A = h \times w_{\frac{1}{2}}$$

where h is the peak height and $w_{\frac{1}{2}}$ is the peak width at half height. Duplicates were made of each run. The area of each component relative to the area of the internal standard, ethyl phthalate, was calculated. This data is presented in Table XIII. A calibration curve was constructed by plotting the relative areas of each component vs its known molarity. A good straight line was obtained as illustrated in Figure XI.

TABLE XIII

CONTROL ANALYSES OF THE PRODUCTS OF METHANOLYSIS OF PHENACYLETHYLMETHYLSULFONIUM PERCHLORATE WITH ADDED 2,6-LUTIDINE

Control	[Methyl Benzoate]	Rel. Area Methyl Benzoate	[Acetophenone]	Rel. Area Acetophenone
2-19-80-1	0.060	1.1250	0.060	1.0180
2-19-67-1	0.050	0.7383	0.050	0.7774
2-19-50-1	0.038	0.6731	0.038	0.5882
2-19-33-1	0.025	0.4489	0.025	0.3884
2-19-20-1	0.015	0.2407	0.015	0.2459
2-19-10-1	0.0075	0.1340	0.0075	0.1173

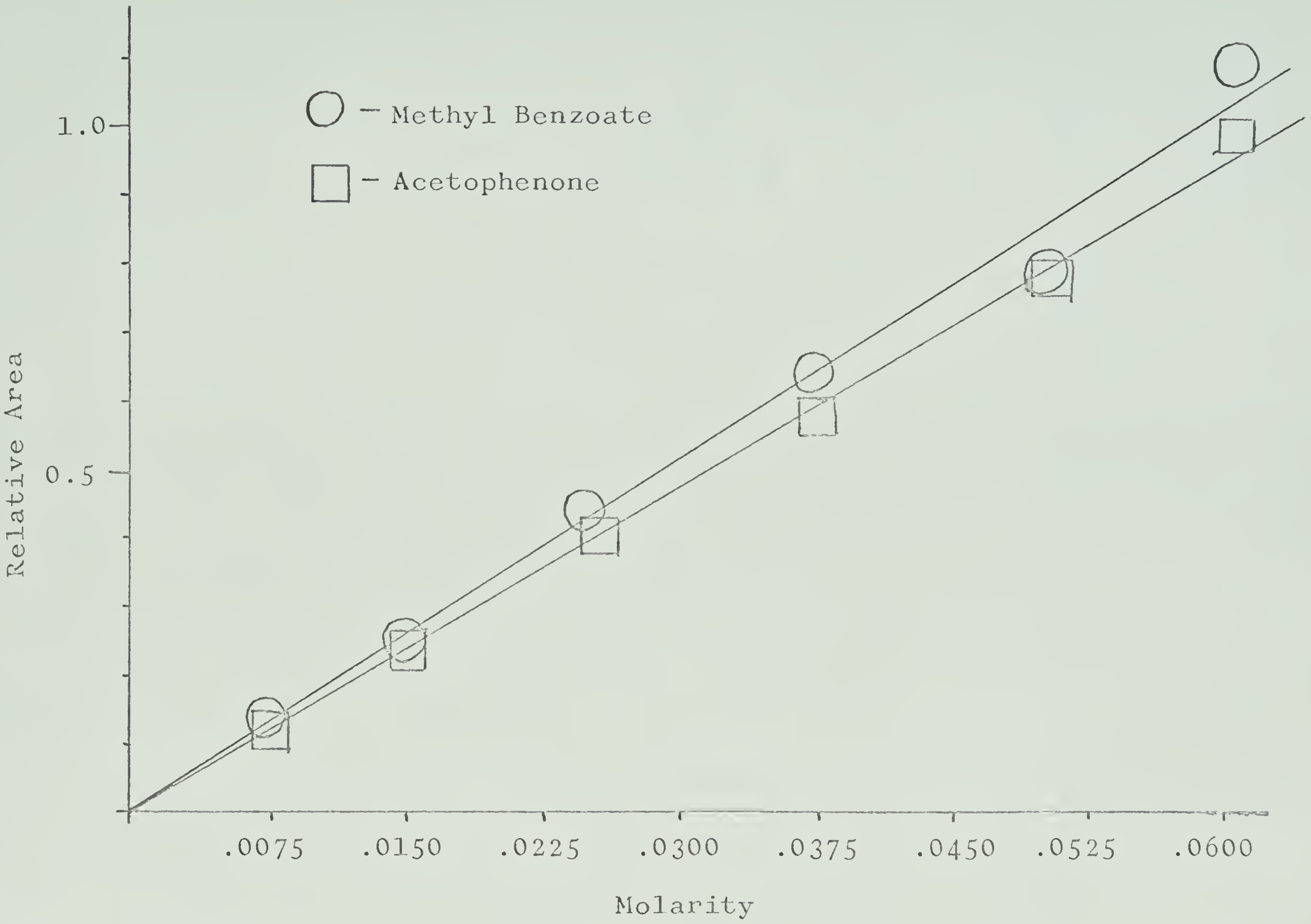


Figure XI. Calibration curve for the product analysis of the methanolysis of phenacylethylmethylsulfonium perchlorate with added 2,6-lutidine Run 2-19.

PRODUCT ANALYSES RUN 2-21

A 0.5896 gm. quantity of phenacylethylmethylsulfonium perchlorate was added to a tared 100 ml. volumetric flask. Enough solvent (ca. 50 ml.) to dissolve the salt was added to the flask, and the contents shaken vigourously until all the salt was dissolved. The solution was diluted to the mark with anhydrous methanol, and the solution equilibrated by shaking the flask 50 times, thus giving a 0.02 M solution of the sulfonium salt in methanol. Aliquots of the solution were transferred to ampoules, the ampoules sealed, and then placed in a constant temperature oil bath at 90.00 ± 0.02° for 76 days, 7-8 half-lives of solvolysis. After removing the ampoules from the oil bath, they were equilibrated to 25°, opened, and a 20.01 ml. aliquot transferred to a round bottomed flask. A 5 ml. aliquot of 0.08 M 2,6-lutidine in methanol was added to neutralize any perchloric acid present in the solution, and then solvent and volatile materials were slowly removed on a rotary evaporator. The residue was taken up in 5.002 ml. of carbon tetrachloride, 0.0404 M in ethyl phthalate. This procedure results in the final concentration of the components being four times greater than the concentration before workup. Aliquots (50 μl) of this solution were injected into the gas chromatographic apparatus using the same conditions as for the control runs.

The peak areas of the components relative to the internal standard, ethyl phthalate, were calculated and the con-

centration of each component obtained by interpolation on the standardization curve (Figure X). The mole per cent of each component was calculated by dividing the concentration of each component by four times the initial concentration of phenacylethylmethylsulfonium perchlorate (0.08 M) and multiplying by 100. It was found that 2-methylthioacetophenone and 2-ethylthioacetophenone were formed in 47 and 18 mole per cent respectively.

PRODUCT ANALYSES RUN 2-31

A 0.02 M solution of phenacylethylmethylsulfonium perchlorate in anhydrous methanol containing 2,6-lutidine (0.06 M) was prepared as previously described. The solution was transferred to a pressure bottle and maintained at a temperature of 90.00 ± 0.02^{o} for 19 days, 10-11 half-lives of solvolysis. On removal from the bath, the solution was equilibrated to 25^{o} and a 9.868 ml. aliquot taken to dryness on a rotary evaporator. The residue was taken up in 2.156 ml. of 0.0404 M ethyl phthalate in carbon tetrachloride. Aliquots (50 μl) of this solution were injected into the gas chromatographic apparatus, employing the same conditions as for the control runs.

The peak areas of the components relative to the internal standard, ethyl phthalate, were calculated and the concentration of each component obtained by interpolation on the standardization curves (Figures X and XI). The mole per

cent of each component was calculated by dividing the concentration of each component by $\frac{9.868}{2.156}$ times the initial concentration of the sulfonium salt and multiplying by 100. 2-Methylthioacetophenone, 2-ethylthioacetophenone, methyl benzoate and acetophenone were found to be formed in 11, 8, 20 and 11 mole per cent respectively.

ANALYSIS FOR ETHYL METHYL SULFIDE FROM THE METHANOLYSIS OF PHENACYLETHYLMETHYLSULFONIUM PERCHLORATE RUN 2-25

A 0.02 M solution of phenacylethylmethylsulfonium perchlorate in anhydrous methanol was prepared and maintained at a temperature of $90.00 \pm 0.02^{\circ}$ for 80 days (*ca*. 8 half-lives of solvolysis). An aliquot of the solution was removed from the bath, equilibrated to 25°, and a 50 μl aliquot of the solution injected directly into the gas chromatographic apparatus. A 20 per cent Carbowax 1500 on 60-80 mesh Chromosorb W column ($6' \times \frac{3}{8}''$) was employed, with a helium flow rate of 55 cc./minute and a column temperature of 63°.

One drop of ethyl methyl sulfide was added to 5 ml. of the above solution, and the resulting solution injected directly into the gas chromatographic apparatus using the same conditions as outlined above.

A solution of ethyl methyl sulfide in methanol (one drop in 5 ml.) was prepared and injected as above.

A comparison of the spectra showed that less than 1 per

cent of ethyl methyl sulfide was formed in the solvolysis of phenacylethylmethylsulfonium perchlorate.

ULTRAVIOLET SPECTRA OF PHENACYLETHYLMETHYLSULFONIUM PERCHLORATE IN METHANOL IN THE PRESENCE OF VARYING CONCENTRATIONS OF PERCHLORIC ACID

A solution of 1×10^{-2} M phenacylethylmethylsulfonium perchlorate in anhydrous methanol was prepared. Aliquots (1 ml.) of this solution were placed in 100 ml. tared volumetric flasks, together with the appropriate amount of 1.5×10^{-3} M perchloric acid in methanol. Each solution was diluted to the mark with anhydrous methanol, followed by equilibration by shaking the flask 50 times. Ultraviolet spectra were taken of each solution and accurate absorbance values obtained at $\lambda_{max} = 250$ mμ. The solutions and absorbance values are listed below.

Solution	Sulfonium Salt	Perchloric Acid	$A_{250\ m\mu}$	log ϵ
A	1×10^{-4}	---------	1.07	4.03
B	1×10^{-4}	1.5×10^{-5}	1.36	4.13
C	1×10^{-4}	1.5×10^{-3}	1.39	4.14

ULTRAVIOLET SPECTRA OF PHENACYLETHYLMETHYLSULFONIUM PERCHLORATE IN METHANOL IN THE PRESENCE OF VARYING CONCENTRATIONS OF SODIUM METHOXIDE

A solution of 2.5×10^{-3} M phenacylethylmethylsulfonium perchlorate in methanol was prepared. Aliquots (1 ml.) of this solution were placed in 25 ml. tared volumetric flasks, together with the appropriate amount of 0.035 M sodium methoxide in methanol. Each solution was diluted to the mark with methanol and equilibrated by shaking the flask 50 times. Ultraviolet spectra were taken of each solution and accurate absorbance values obtained at $\lambda = 297$ mμ. The solutions and absorbance values are listed below.

Solution	Sulfonium Salt	Sodium Methoxide	$A_{297\ m\mu}$	$\log \epsilon$
A	1×10^{-4}	5×10^{-5}	0.614	3.79
B	1×10^{-4}	1×10^{-4}	0.918	3.96
C	1×10^{-4}	1.5×10^{-4}	0.985	3.99
D	1×10^{-4}	2×10^{-4}	0.999	4.00
E	1×10^{-4}	6×10^{-4}	0.998	4.00

CHAPTER II

ETHYLMETHYLSULFONIUM PHENACYLIDE

Stable sulfonium ylides have been known since 1935, when Hughes and Kuriyan (36) isolated dimethylsulfonium 9-fluorenylide. A number of isolable sulfonium ylides have been prepared since that time, but it was not until 1966 that sulfonium ylides stabilized by only one carbonyl group were isolated. In that year, Ratts and Yao (27) isolated a number of sulfonium ylides of the general formula $(CH_3)_2S^+-\overset{-}{C}HCOR$, by treating the appropriate sulfonium salt with base.

The structure of sulfonium ylides has been quite well established, and has been shown to be pyramidal in nature. This conclusion was made on the basis of non-equivalence of $S-CH_2$ protons in the nuclear magnetic resonance spectra (37) and X-ray crystalography studies (39).

A study of the racemization of ethylmethylsulfonium phenacylide was undertaken to gain further insight into the requirements and limitations of pyramidal inversion as a mechanism for racemization. The synthesis of the racemic and optically active ylide will be discussed as well as the rates of racemization in various solvents and at various temperatures.

SYNTHESIS

Ethylmethylsulfonium phenacylide was prepared as illustrated

in Figure XII by a method analogous to that described by Ratts and Yao (27) for the synthesis of similar sulfonium ylides. The method employed consisted of treating the sulfonium salt with an excess of base, extraction of the ylide thus formed with chloroform, and subsequent evaporation of the chloroform to yield the ylide. At all times the ylide was kept in the dark and under a nitrogen atmosphere.

Racemic ethylmethylsulfonium phenacylide was prepared directly from racemic phenacylethylmethylsulfonium bromide, whereas the optically active isomer was prepared from (-)-phenacylethylmethylsulfonium perchlorate. The change in specific rotation with change in incident wavelength for (-)-ethylmethylsulfonium phenacylide in solvent benzene is illustrated in Figure XIII.

The n.m.r. spectrum of the ylide showed non-equivalence of the methylene protons of the ethyl group. The signals for the two protons are separated by _ca_. 60 cps. Each proton is coupled with the protons of the adjacent methyl group, and also with the other proton of the methylene group. This gives rise to a complex multiplet signal, probably an octet. As explained in Chapter I when discussing the n.m.r. spectrum of phenacylethylmethylsulfonium bromide, the differentiation of these protons is expected since they are adjacent to an asymmetric center.

The structure of ethylmethylsulfonium phenacylide was assigned on the basis of a comparison of its n.m.r. and

infrared spectra in $CDCl_3$ and CCl_4 respectively, with those reported by Ratts and Yao (27) for similar compounds. Its elemental analysis was also satisfactory. Conclusive proof of structure was its n.m.r. spectrum in CF_3COOH, which was the same as that of phenacylethylmethylsulfonium perchlorate in the same solvent. Structure assignment is discussed in more detail in the Discussion section. Details of the synthesis and properties of ethylmethylsulfonium phenacylide are presented in the Experimental section.

RACEMIZATION STUDIES

Racemization rates were studied by following the disappearance of optical rotation vs time. A Perkin-Elmer Model 141 Polarimeter was used, using incident light 589 mμ. The entire reaction was studied in a thermostated polarimeter tube. The rotations were obtained directly from the digital readout of the instrument, with infinity measurements being taken after ten half-lives of racemization. The first-order rate constants were calculated from the relationship:

$$k = \frac{2.303}{t} \log \frac{\alpha_\infty - \alpha_o}{\alpha_\infty - \alpha_t}$$

where α_o is the initial rotation and α_t is the rotation at time t. Reactions were followed to 75-85 per cent completion, and a good straight line was obtained when $(\alpha_\infty - \alpha_t)$ was plotted vs time. A typical rate analysis, Run 1-215, is shown

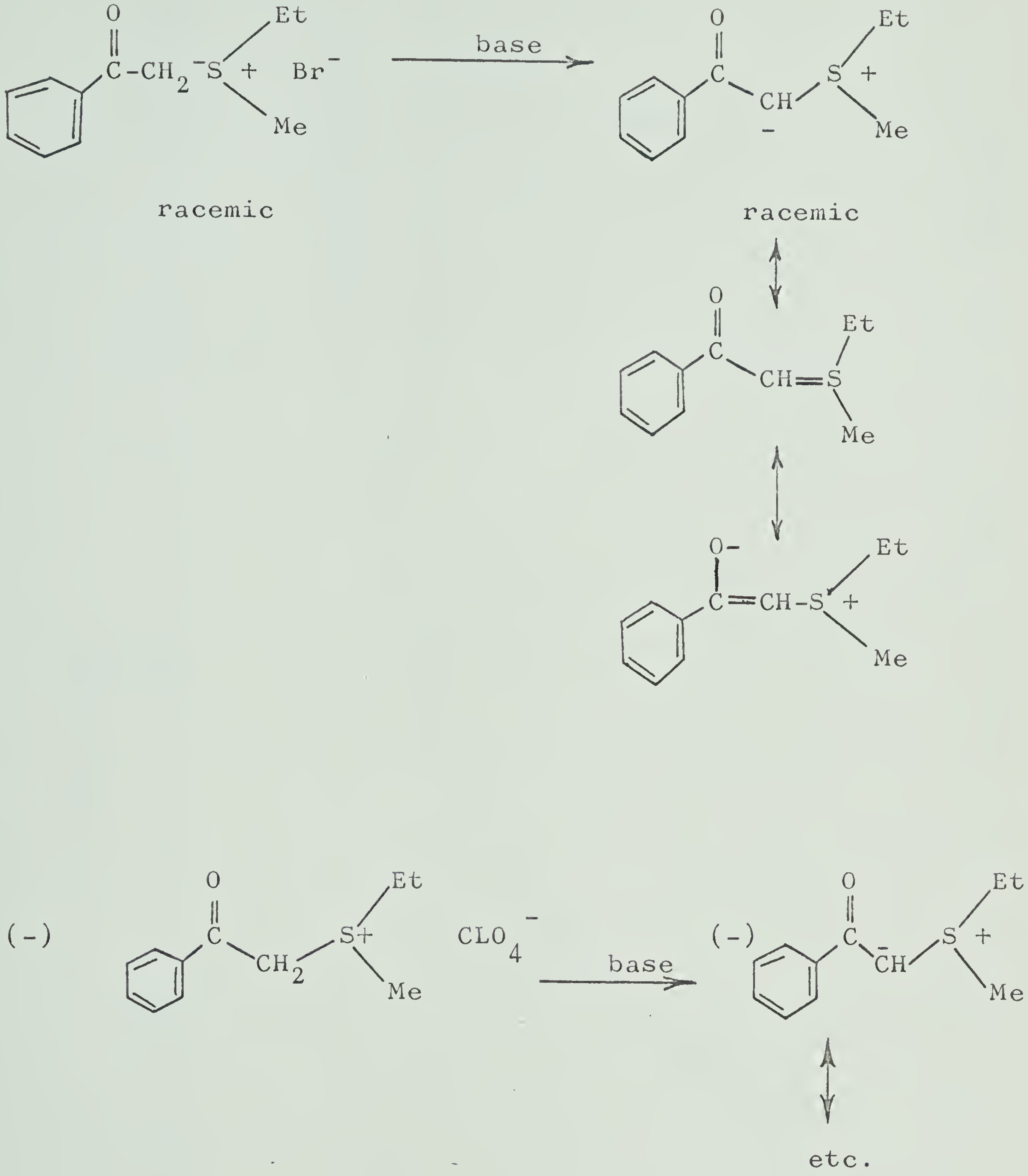


Figure XII. Synthesis of Ethylmethylsulfonium phenacylide

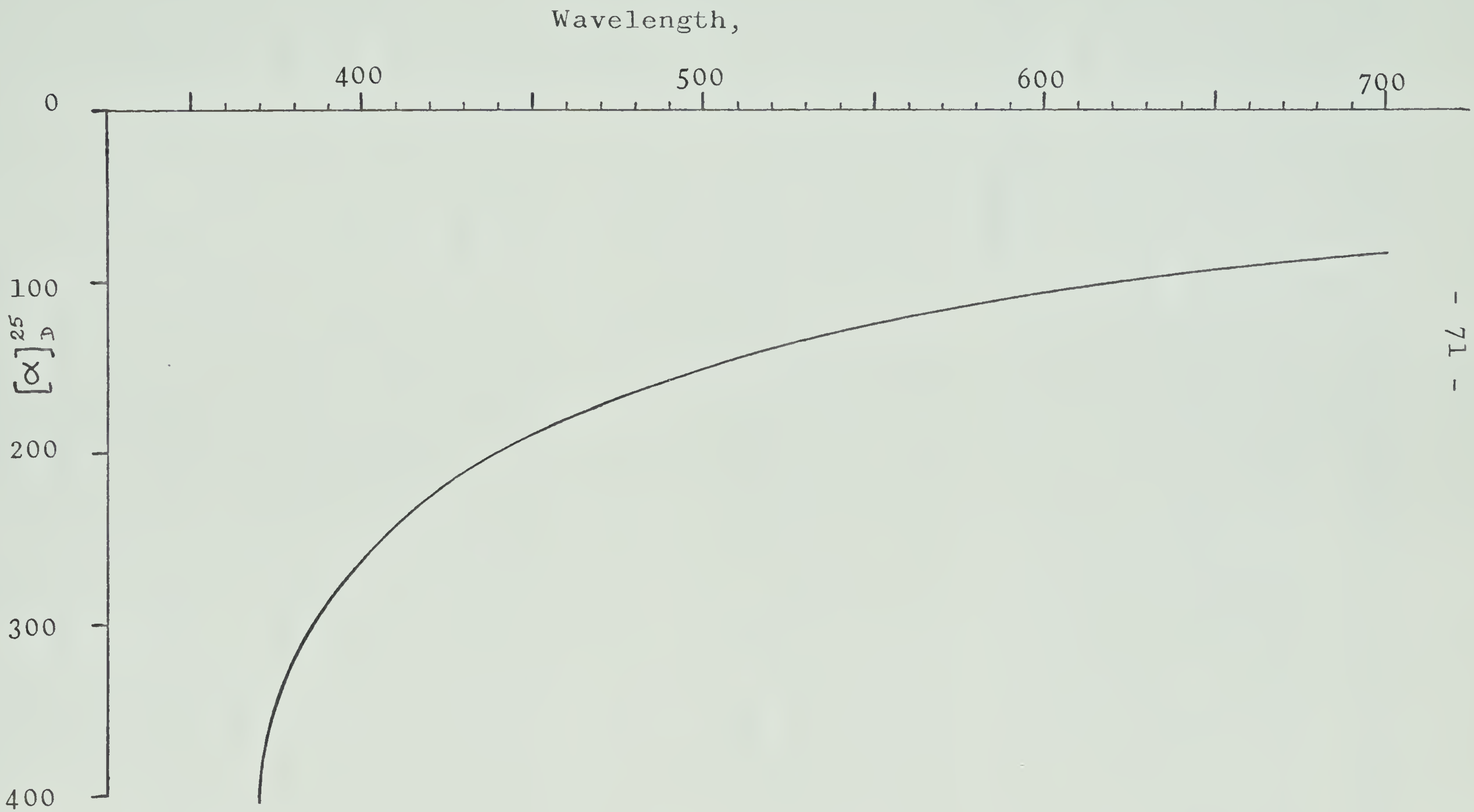


Figure XIII. Specific rotation of (-)-Ethylmethylsulfonium Phenacylide vs. wavelength of incident light. (Solvent : Benzene)

in Table XIV with the corresponding plot of log $(\alpha_\infty - \alpha_t)$ vs time illustrated in Figure XIV.

Table XV summarizes the racemization rates which were run on (-)-ethylmethylsulfonium phenacylide. The specific first-order rate constants for the conversion of one enantiomer to the other, k_1, are also presented.

DECOMPOSITION STUDIES

Decomposition of ethylmethylsulfonium phenacylide in carbon tetrachloride (accomplished by maintaining the solution at $50.00 \pm 0.02^\circ$ for ten days) results in the formation of 67 mole per cent 2-methylthioacetophenone. The rest of the products were not identified.

DISCUSSION

Nuclear magnetic resonance spectral data for ethylmethylsulfonium phenacylide (I) and dimethylsulfonium phenacylide (II), the latter synthesized by Ratts and Yao (27), are presented in Table XVI. From an examination of this table it is seen that in the corresponding solvents the two compounds display strikingly similar n.m.r. chemical shifts for similar groups. The n.m.r. spectrum obtained by dissolving the ylide I in CF_3COOH is almost identical with that of the sulfonium salt in the same solvent. The two spectra would not be the same if basic treatment of the sulfonium salt had resulted in the formation of a compound with a rearranged

TABLE XIV

RACEMIZATION OF 0.044 M (-)-ETHYLMETHYLSULFONIUM PHENACYLIDE IN CARBON TETRACHLORIDE AT 25.00° RUN 1-215.

Time (10^4 sec)	α_D^{25}	log $(\alpha_\infty - \alpha_t)$	$10^5 k_\alpha$ (sec^{-1})
0	-0.148	$\bar{1}.170$	—
1.35	-0.126	$\bar{1}.100$	1.19
3.60	-0.090	$\bar{2}.954$	1.38
4.32	-0.082	$\bar{2}.914$	1.37
8.49	-0.048	$\bar{2}.681$	1.33
10.08	-0.040	$\bar{2}.602$	1.30
11.01	-0.034	$\bar{2}.531$	1.33
14.28	-0.023	$\bar{2}.362$	1.30
95.85	0.000	Average	1.34 ± 0.03

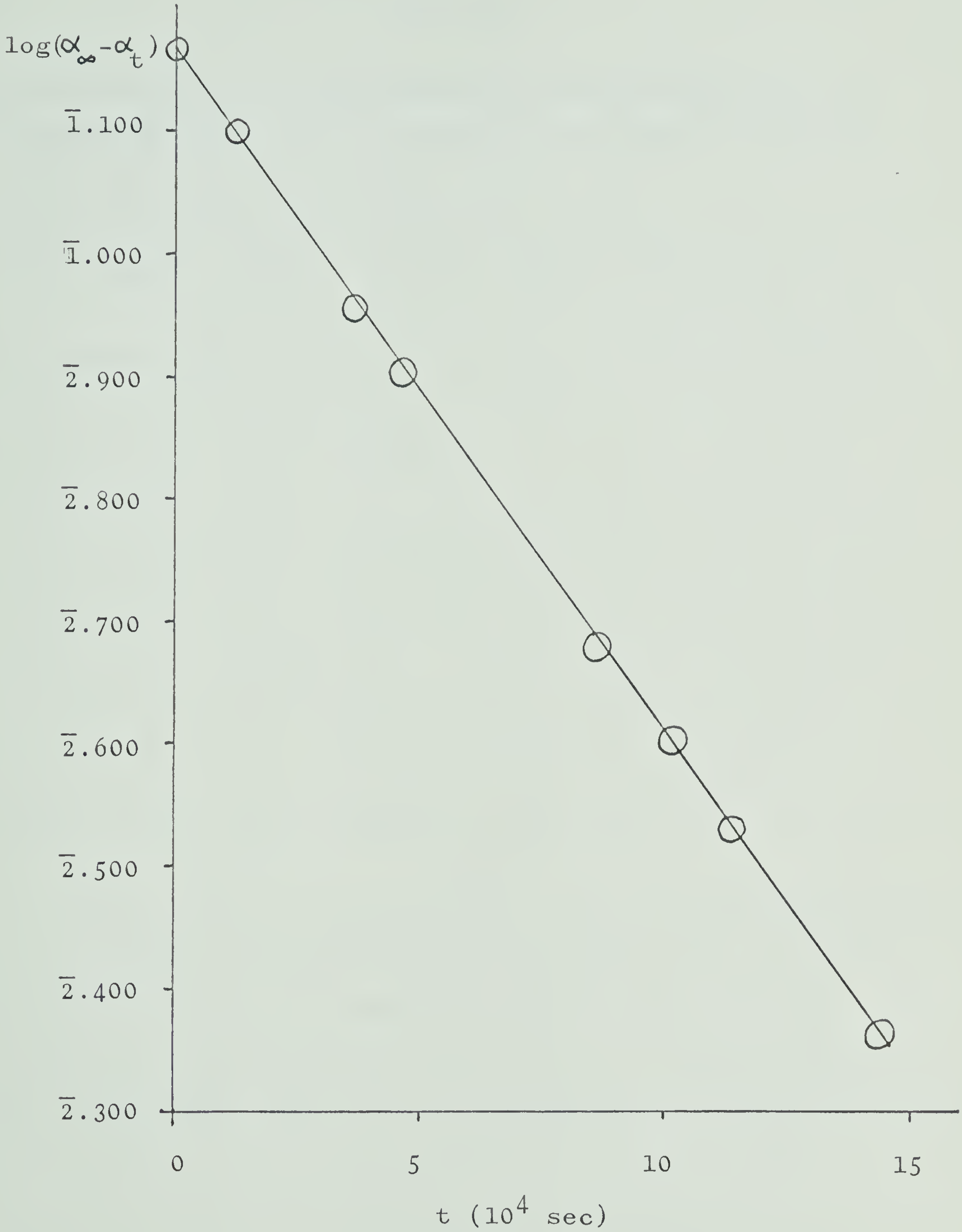


Figure XIV. Racemization of 0.044 M (-)-ethylmethylsulfonium phenacylide in carbon tetrachloride at 25.00° Run 1-215.

TABLE XV

RACEMIZATION OF (-)-ETHYLMETHYLSULFONIUM PHENACYLIDE IN VARIOUS SOLVENTS AT 25.00° AND 50.00° USING AN INCIDENT LIGHT WAVELENGTH OF 589 mμ

Run	Isomer	[I]	Solvent	Temp.	10^5 k_α (sec^{-1})	10^5 k_1 (sec^{-1})
1-227	(-)	.0235	CH_2Cl_2	25	3.52 ± .05	1.76 ± .03
1-223	(-)	.021	Benzene	25	1.67 ± .01	0.83 ± .01
1-215	(-)	.044	CCl_4	25	1.34 ± .03	0.67 ± .02
1-206	(-)	.018	Benzene	50	39.7 ± 0.2	19.8 ± 0.1
1-203	(-)	.025	CCl_4	50	30.7 ± 0.4	15.3 ± 0.2
1-211	(-)	.0245	CCl_4	50	28.4 ± 1.1	14.2 ± 0.6
1-147[1]	(-)	.030	Methanol	50	75.0 ± 1.7	37.5 ± 0.9
2-53[1]	(-)	.030	Methanol	50	71.6 ± 1.8	35.8 ± 0.9
2-55[2]	(-)	.106	Benzene	50	41.8 ± 0.2	20.9 ± 0.1

1) These runs were made by dissolving the appropriate amount of (-)-phenacylethylmethylsulfonium perchlorate in methanol with the appropriate amount of added sodium methoxide. Run 1-147 is 0.090 M and Run 2-53 is 0.21 M in sodium methoxide.

2) An incident light having a wavelength of 436 mμ was used.

TABLE XVI

NUCLEAR MAGNETIC RESONANCE SPECTRAL DATA FOR ETHYLMETHYLSULFONIUM PHENACYLIDE AND DIMETHYLSULFONIUM PHENACYLIDE

Com'd	Nmr Chemical Shifts (Area)					
	CH_3-S^1	$CH_3\underline{CH}_2$-S^2	$\underline{CH}_3CH_2$-S^3	Ar^4	Ar-CO-$\underline{CH}$	Solvent
I	7.2(3)	6.15(1) 7.15(1)	8.77(3)	2.43(5)	5.8(1)	$CDCl_3$
II	7.2(6)	------	------	2.44(5)	5.25(1)	$CDCl_3$
I	6.91(3)	6.43(2)	8.38(3)	2.20(5)	4.77(2)	CF_3COOH
II	6.95(6)	------	------	2.37(5)	4.83(2)	CF_3COOH

1) Singlet

2) Multiplet centered at value shown

3) Triplet centered at value shown

4) Multiplet centered at value shown

skeleton. The fact that they are the same is therefore conclusive confirmation of the ylide structure. The only difference in the two spectra is the chemical shift of the signal for the methylene protons of the phenacyl moiety. It was located at τ 4.77 for the ylide and at τ 4.75 for the sulfonium salt. This small difference may be due to the slightly different environment created by the perchlorate anion.

As seen from Table XVI the n.m.r. spectrum of ethylmethylsulfonium phenacylide shows non-equivalent methylene protons. In fact their chemical shifts are 60 cps apart. The signals for these protons have been reported as multiplets, whereas they are probably octets caused by each proton coupling with the adjacent methyl protons as well as with each other. The reason for the non-equivalence is the asymmetric sulfur center as explained previously.

A further comparison of compounds I and II showed that they both have carbonyl stretching frequencies of 1520 cm^{-1}, whereas their corresponding sulfonium salts have infrared carbonyl stretching frequencies of ca.1670 cm^{-1}.

As mentioned in the Synthesis section, ethylmethylsulfonium phenacylide gave a satisfactory analysis. This, as well as the above evidence, indicated that the synthesized compound was indeed ethylmethylsulfonium phenacylide.

Ethylmethylsulfonium phenacylide racemizes 200 times faster than phenacylethylmethylsulfonium perchlorate in

methanol at 50° (Cf. Runs 1-147 and 1-249, Table VII). The effect of solvent on the racemization rate of the ylide is very small, since the rate in methanol (Dielectric constant 33.6) is only twice that in carbon tetrachloride (Dielectric constant 2.24) at 50° (Table XV). Independent control studies, Runs 2-41 and 1-211, establish that loss of optical activity by the ylide is due to racemization and not decomposition of the substrate. Product studies indicate that decomposition of the ylide, resulting in the formation of 67 mole per cent 2-methylthioacetophenone, occurs for the most part by a pathway other than breakage of the phenacyl-sulfur bond.

Carbon-sulfur bond heterolysis to form a carbene and ethyl methyl sulfide, with subsequent recombination to form the racemic ylide is a possible mechanism which could account for racemization without decomposition. However, this is highly unlikely in view of the fact that 2-methylthioacetophenone, not a carbene reaction product, accounts for 67 mole per cent of the decomposition products. This view is further substantiated by work carried out by Nozaki _et_ _al_ (37c) on phenylmethylsulfonium phenacylide. Heating this ylide with sulfides other than phenyl methyl sulfide produced no sulfide exchange. In addition, formation of the ylide from the sulfonium salt in solutions containing other sulfides produced no exchanged ylides.

The only reasonable mechanism which accounts for racemization without decomposition is pyramidal inversion.

ACTIVATION PARAMETERS

To determine the effect of temperature on racemization of ethylmethylsulfonium phenacylide, calculations similar to those described in Chapter I were made. The values calculated for the enthalpy and entropy of activation for the racemization of the ylide in carbon tetrachloride and benzene are as follows:

Benzene: $\Delta H^{\ddagger} = 23.6 \pm 0.2$ kcal/mole

$\Delta S^{\ddagger} = -1.1 \pm 0.5$ e.u.

Carbon tetrachloride: $\Delta H^{\ddagger} = 23.3 \pm 0.3$ kcal/mole

$\Delta S^{\ddagger} = -2.8 \pm 0.8$ e.u.

We will now consider why the sulfonium ylide racemizes so much faster than its sulfonium salt analog. The lone pair of electrons on the sulfur atom will have more s-character in the sulfonium salt than in the corresponding ylide, since the phenacylide group is more electropositive than the phenacyl group (33). As a result, the sulfur-alkyl bonds will have more p-character in phenacylethylmethylsulfonium perchlorate than in ethylmethylsulfonium phenacylide. This will result in the ylide having a more nearly planar configuration than the sulfonium salt. Since the transition state for pyramidal inversion is indeed planar, one would expect that the energy of activation would be correspondingly less

for the ylide than the sulfonium salt, enabling it to racemize faster by this mechanism. Another possibility is that p-d π bonding might be better at the transition state for the ylide than at the ground state. Since the sulfonium salt is incapable of this type of stabilization of the transition state, this may also explain the faster rate of racemization for the ylide.

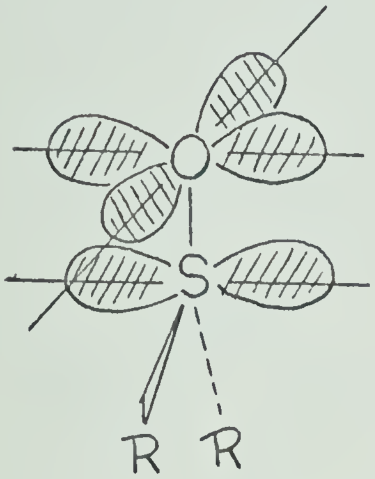
Sulfoxides are somewhat similar to ylides in structure in that they also have a negative charge on the center adjacent to sulfur. On the basis of the foregoing reasoning, one might expect them to racemize with a rate at least comparable in magnitude to that of the ylides. This is not the case, however, since Mislow and co-workers (29) have shown that pyramidal inversion in a number of aryl sulfoxides is an extremely slow process at ordinary temperatures, having an activation enthalpy of ca. 40 kcal/mole.

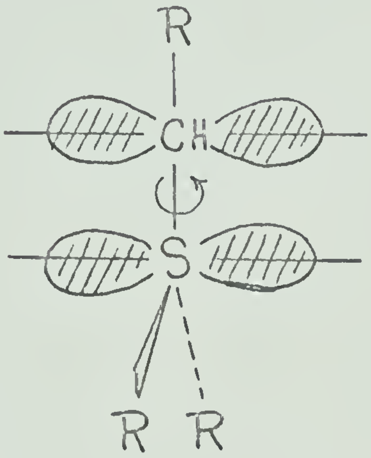
There are a number of factors which could contribute to the enormous difference in activation enthalpies for inversion of the ylide I and the sulfoxides. In any molecule where sulfur is surrounded by groups in a tetrahedral arrangement, π-bonding can occur between suitable orbitals of the surrounding groups and the sulfur orbitals, $d_{x^2-y^2}$ and d_{z^2} (38). These orbitals are more favourable for π-bonding than the other d-orbitals of sulfur both geometrically and energetically. Consequently, the two lone-pairs of electrons which are located in p-orbitals on the oxygen atom can par-

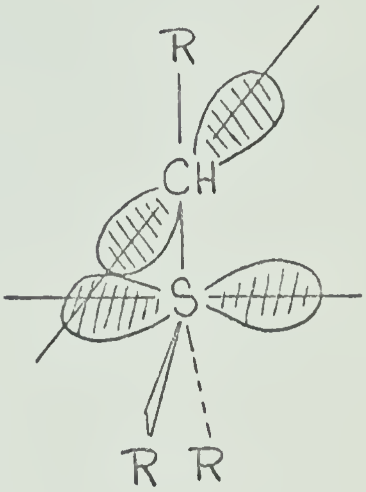
ticipate in p-dπ overlap with the two d-orbitals of the sulfur center in the ground state. In the planar transition state for pyramidal inversion, the two d-orbitals of sulfur which are geometrically most favourable for p-dπ overlap are the d_{xz} and the d_{xy} orbitals. However, the d_{xy} orbital is higher in energy than the d_{xz} orbital. This may result in p-dπ overlap between the oxygen and the sulfur to be more favourable in the ground state than in the transition state, thereby stabilizing the ground state relative to the transition state. Since the ylide has only one pair of non-bonding electrons on the center adjacent to the sulfur atom, p-dπ overlap should be at least as favourable in the transition state as in the ground state.

Griffith and Roberts (30) found that N-benzyl-N,O-dimethylhydroxylamine underwent very slow pyramidal inversion compared to simple tertiary amines. They felt that this was due to destabilization of the transition state relative to the ground state, caused by electronic repulsion between the lone-pairs on oxygen and that on nitrogen. A similar argument may be invoked to account for the slow inversion of sulfoxides. If we assume sulfur to be sp^3 hybridized in the ground state and sp^2 hybridized in the transition state, then in the transition state there are more severe electronic interactions between the lone-pair on sulfur and the two lone-pairs on oxygen (all in p-orbitals). The ylide, which has only one lone-pair of electrons on the center ad-

jacent to the sulfur atom, will not experience such severe electrostatic interactions in the transition state since the two lone-pairs may be arranged at right angles to each other, where electronic repulsion will be at a minimum.

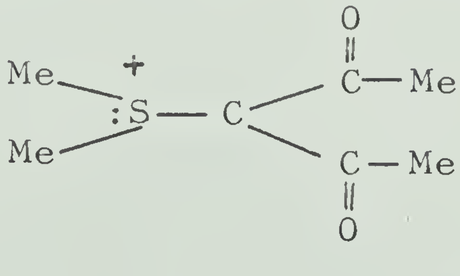






One would expect this to be the preferred conformation by analogy to the hydrazines, where it has been shown that the lone pairs on the nitrogen atoms are indeed at right angles to each other (32). The sulfoxides are susceptible to both destabilization of the transition state and stabilization of the ground state relative to the ylide, and this would account at least partly for the appreciable difference in their activation enthalpies.

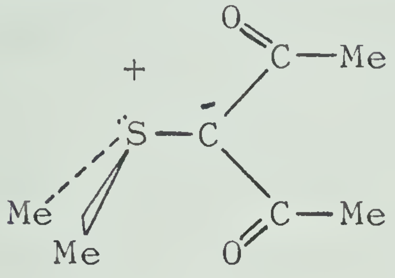
Nozaki et al (37c) have recently reported an n.m.r. spectral study of dimethylsulfonium diacetylmethylide, compound III.



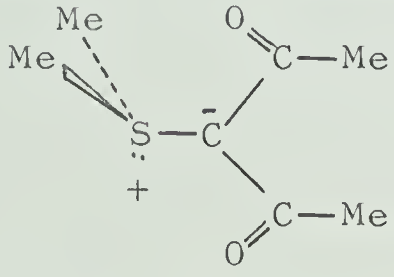
$$(\mathrm{Me})_2\overset{+}{\ddot{\mathrm{S}}}-\mathrm{C}(\mathrm{C}(=\mathrm{O})\mathrm{Me})_2$$

III

This compound exhibited magnetic equivalence of the two C-Me groups at room temperature. However, they became differentiated at lower temperatures, the coalescence temperature being ca. -25°. They interpreted their observations by assuming a rapid exchange between IIIa and IIIb at room temperature, with the exchange slowed down considerably at lower temperatures. Their calculations showed that the average lifetime of each conformer was ca. 0.02 seconds.



IIIa

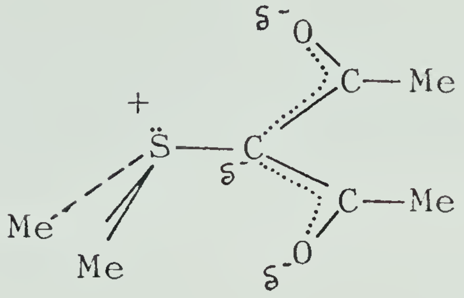


IIIb

This exchange may occur by either rotation about the S-C bond or pyramidal inversion of the sulfur atom. These workers suggested that the latter is the more plausible mechanism of the two.

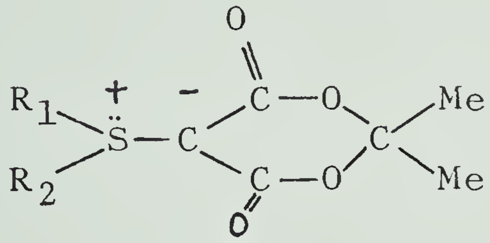
In view of our present results, it seems highly unlikely that pyramidal inversion in this system could be occurring at such a rapid rate. However, one might be able to rationalize it on the following basis. In the ylide III, the carbon adjacent to sulfur is bonded to two carbonyl groups. If this group is much larger sterically than a phenacylide group in which carbon is bonded to a carbonyl and a hydrogen, then there would be steric acceleration of the rate caused by relief of non-bonded interactions in going from the ground state to the transition state. Another possible explanation

is electronic in nature. Since the carbonyl groups each carry a partial negative charge in the carbanion,



the oxygens might tend to arrange themselves as close as possible to the positive sulfur center. This might force the two S-Me groups into a more planar arrangement, thereby lowering the activation energy for pyramidal inversion. Either or both of the above factors might result in an extremely fast pyramidal inversion of the ylide III.

Hochrainer and Silan (37b) have recently reported an investigation of sulfonium ylides of the following structure:



IV

a) $R_1 = C_6H_5CH_2$, $R_2 = C_6H_5CH_2$

b) $R_1 = C_6H_5CH_2$, $R_2 = CH_3$

c) $R_1 = C_2H_5$, $R_2 = C_2H_5$

The n.m.r. spectra showed the methylene protons of the R groups to be non-equivalent at room temperature. For IVa non-equivalence of the methylene protons is exhibited up to temperatures of at least 100°. This can only be explained if pyramidal inversion is not extremely rapid in these systems.

This evidence indicates that the equivalence at room temperature of the C-Me groups in III is due not to rapid

pyramidal inversion about the sulfur center, but rather to a simple rotation about the C-S bond. This rotation would be slowed down considerably at -25°, thus causing magnetic non-equivalence of the C-Me groups to be exhibited below this temperature.

EXPERIMENTAL

SOLVENTS

Benzene

Shawinigan Reagent Grade benzene was purified according to the method described by Fieser (34) by treating it with conc. sulfuric acid. The treated solvent was fractionally distilled (b.p. 79° at 708 mm.) from calcium hydride and stored in a tightly-stoppered dark bottle.

Carbon tetrachloride

Shawinigan Reagent Grade carbon tetrachloride was purified according to the method described by Fieser (35) by treating it with concentrated potassium hydroxide in methanol, and then conc. sulfuric acid. The treated solvent was distilled (b.p. 76° at 700 mm.) from phosphorous pentoxide and stored in a tightly-stoppered dark bottle.

Methylene chloride

Fisher Certified methylene chloride was treated successively with $\frac{1}{10}$ volume of conc. sulfuric acid and $\frac{1}{2}$ volume of water three times. The solvent was then washed with dilute potassium carbonate and twice with water. It was dried with $MgSO_4$ and then fractionally distilled (b.p. 40° at 700 mm.), and stored in a tightly-stoppered dark bottle.

REAGENTS AND MATERIALS

(dl)-Ethylmethylsulfonium phenacylide

(dl)-Ethylmethylsulfonium phenacylide was prepared according to the method described by Ratts and Yao (27) for preparing dimethylsulfonium phenacylide by treating phenacylethylmethylsulfonium bromide (11.04 gm., 0.04 moles) with 200 ml. of a 5 per cent sodium hydroxide solution (0.25 moles) at 5°. The resulting solution was stirred under nitrogen for 15 minutes. This solution was extracted several times with chloroform, the combined extracts washed twice with water, dried with magnesium sulfate and the chloroform removed on a rotary evaporator. The resulting yellow oil was found to crystallize on drying in vacuo. These crystals were recrystallized from benzene-Skelly Solve B to yield 3.27 gm. (42 per cent) of pure ethylmethylsulfonium phenacylide, which was stored under nitrogen in the refrigerator. M.p. 83-85°. N.m.r. ($CDCl_3$): τ 2.43 (m, 5H), 5.86 (s, 1H), 5.8-6.5 (m, 1H), 6.8-7.5 (m, 1H), 7.20 (s, 3H), 8.77 (t, J = 7.5 cps, 3H). (Note that the two protons of the methylene group of the ethyl moiety are differentiated into two multiplet signals, τ 5.8-6.5 and 6.8-7.5. These two regions also contain the signals for the methine group and the methyl group bonded to the sulfur center. The n.m.r. integration of each region naturally included these groups; the integration reported above has been separated into components for convenience only.) Infrared: 3080-3010 (several),

2970-2880 (several), 1580, 1520, 1370, 1290, 1200, 1085, 1060, 1020, 960 and 850 cm^{-1}.

Anal. Calcd. for $C_{11}H_{14}OS$: C, 68.00 ; H, 7.26 ; S, 16.50

Found: C, 67.99, 68.06; H, 7.13, 7.33; S, 15.99, 16.47.

(-)-Ethylmethylsulfonium phenacylide

(-)-Phenacylethylmethylsulfonium perchlorate (14.3 gm., 0.048 moles) was treated with 240 ml. of a 5 per cent sodium hydroxide solution (0.030 moles), and the workup conducted in a manner similar to that for the racemic material. Yield: 4.7 gm. (50 per cent), m.p. 83-85°, $[\alpha]_D^{25}$ -137.4 (c = 0.487, benzene). N.m.r. ($CDCl_3$): superimposable on that of (dl)-ethylmethylsulfonium phenacylide. N.m.r. (CF_3COOH): τ 2.2 (m, 5H), 4.77 (s, 2H), 6.43 (m, 2H), 6.91 (s, 3H), 8.38 (t, J = 7.5 cps, 3H), Infrared: superimposable on that of the racemic material.

KINETICS

Polarimetric Rates

(-)-Ethylmethylsulfonium phenacylide was accurately weighed in a tared volumetric flask, enough solvent to dissolve the compound was added and the solution diluted to the mark. The solution was equilibrated by shaking the flask 50 times. An aliquot of the solution was placed in a 1 dm. polarimeter tube surrounded by a water jacket through which water from a constant temperature bath at 50.00 ± 0.02 or 25.00 ± 0.02° was circulated. The polarimeter tube was placed

in the compartment of a Perkin-Elmer Polarimeter Model 141. At appropriate time intervals the optical rotation was obtained directly from the digital readout of the instrument, with "zero" readings being obtained before and after each measurement. The first reading was taken at least 5 minutes after the solution was placed in the tube to ensure temperature equilibration. An incident light beam having a wavelength of 589 mu was employed.

The rate constants were obtained on the basis of the experimental infinity obtained after 10 half-lives of racemization (0.000 ± 0.002). A typical rate analysis has been presented in the Result section.

RACEMIZATION OF (-)-ETHYLMETHYLSULFONIUM PHENACYLIDE RUN 2-41

A solution of 0.1947 gm. of (-)-ethylmethylsulfonium phenacylide in 50 ml. of carbon tetrachloride (α_D^{25} -.533 ± .002) was prepared and placed in a 50.00 ± 0.02° constant temperature bath for 2 hours, 3 half-lives of racemization. On removal from the bath the rotation had decreased to α_D^{25} = -0.067 ± 0.002. The solvent was removed on a rotary evaporator, and the resulting oil dried in vacuo for 24 hours. Yield: 0.1940 gm. (100 per cent). The resulting light yellow crystals had m.p. 83-85°. This, as well as n.m.r. and infrared spectra, indicated that the recovered material was pure ethylmethylsulfonium phenacylide.

RACEMIZATION OF (-)-ETHYLMETHYLSULFONIUM PHENACYLIDE RUN 1-211

A solution of 0.1189 gm. of (-)-ethylmethylsulfonium phenacylide in carbon tetrachloride was prepared. A 1 ml. aliquot of this solution was diluted by a factor of 500 with spectral grade carbon tetrachloride, and an ultraviolet spectrum of the resulting solution obtained using spectral grade carbon tetrachloride as a blank ($\log \epsilon = 3.908$, $\lambda = 318 m\mu$). Another 1 ml. aliquot of the solution was diluted by a factor of 500 with methanol containing perchloric acid such that the resulting molarity of the acid was 1.5×10^{-4} M (3 times the molarity of the substrate), and an ultraviolet spectrum of this solution obtained ($\log \epsilon = 4.157$, $\lambda = 245\ m\mu$). The remaining portion of the initial solution was maintained at 50.00 ± 0.02° for 165 minutes, four half-lives of racemization, when ultraviolet spectra were again taken using the procedure described above ($\log \epsilon = 3.884$, $\lambda = 318\ m\mu$; $\log \epsilon = 4.135$, $\lambda = 245\ m\mu$). The ultraviolet data indicates 4-5 per cent decomposition of the ylide after four half-lives of racemization.

PRODUCT ANALYSES RUN 2-40

A 0.023 M solution of ethylmethylsulfonium phenacylide in carbon tetrachloride was prepared in the usual manner. The solution was transferred to a pressure bottle and maintained at a temperature of 50.00 ± 0.02° for 10 days (n.m.r.

and ultraviolet spectra indicate complete decomposition of starting material). On removal from the bath the solution was equilibrated to 25° and a 25 ml aliquot of the solution taken to dryness on a rotary evaporator. The residue was taken up in 4.934 ml of 0.0404 M ethyl phthalate in carbon tetrachloride. Aliquots (50 ul) of this solution were injected into the gas chromatographic apparatus, employing the same conditions as for the control run (Run 2-35) described in Chapter I.

The peak area of 2-methylthioacetophenone relative to the internal standard, ethyl phthalate, was calculated and the concentration obtained by interpolation on the standardization curve (Figure X). The mole per cent of 2-methylthioacetophenone was obtained by dividing the concentration obtained above by $\frac{25}{4.934}$ times the initial concentration of ethylmethylsulfonium phenacylide and multiplying by 100. It was concluded that complete decomposition of the ylide results in the formation of 67 mole per cent of 2-methylthioacetophenone.

BIBLIOGRAPHY

(1) M. F. Manning: J. Chem. Phys. 3, 136 (1935).

(2) J. F. Kincaid and F. C. Henriques Jr.: J. Am. Chem. Soc. 62, 1474 (1940).

(3) F. T. Wall and G. Glocker: J. Chem. Phys. 5, 314 (1937).

(4) R. E. Weston Jr.: J. Am. Chem. Soc. 76, 2045 (1954).

(5) C. C. Costain and G. B. B. M. Sutherland: J. Phys. Chem. 56, 321 (1952).

(6) W. J. Pope and S. J. Peachy: J. Chem. Soc. 1900, 1072.

(7) S. Smiles: J. Chem. Soc. 1900, 1174.

(8) M. P. Balfe, J. Kenyon and H. Phillips: J. Chem. Soc. 1930, 2554.

(9) D. Darwish and G. Tourigny: J. Am. Chem. Soc. 88, 4303 (1966).

(10) R. Scartazzini and K. Mislow: Tetrahedron Letters, No. 28, 2717 (1967).

(11) D. Darwish and S. H. Hui: 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1967, Abstracts p. 520.

(12) L. F. Fieser: Experiments in Organic Chemistry, 3rd Edition, p.289. D. Heath and Co., Boston (1957).

(13) H. E. Zimmerman: Molecular Rearrangements, p.378. P. de Mayo, Ed., Interscience Publishers, Inc., New York (1963).

(14) K. W. Ratts and A. N. Yao: J. Org. Chem. 33, 70 (1968).

(15) A. A. Frost and R. G. Pearson: Kinetics and Mechanism, p.98-100. John Wiley and Sons, Inc., New York (1953).

(16) (a) American Chemical Society: Specifications 1960: Reagent Chemicals, p.17 Applied Publications, American Chemical Society, Washington, D.C. (1961).

(b) J. Mitchell Jr. and D. M. Smith: Aquametry, Ch. 5, Interscience Publishers, Inc., New York (1948).

(17) S. G. Smith, A. H. Fainberg and S. Winstein: J. Am. Chem. Soc. 83, 624 (1961).

(18) C. L. Butler and L. H. Cretcher: J. Am. Chem. Soc. 55, 2605 (1933).

(19) L. F. Fieser: Experiments in Organic Chemistry, 3rd Edition p. 291. D. Heath and Co., Boston (1957).

(20) H. C. Brown, S. Johnson and H. Podell: J. Am. Chem. Soc. 76, 5556 (1954).

(21) W. E. McEwen, D. M. Coyne and C. A. Vanderwerf: J. Am. Chem. Soc. 78, 3061 (1956).

(22) C. Wahl: Ber. 55, 1449 (1922).

(23) K. Griesbaum, A. A. Oswald and B. E. Hudson: J. Am. Chem. Soc. 85, 1969 (1963).

(24) L. Higginbotham, A. Lapworth and C. Simpson: J. Chem. Soc. 125, 2339 (1924).

(25) V. Prelog, V. Hahn, H. Brauchli and H. C. Beyerman: Helv. Chim. Acta. 27, 1209 (1944).

(26) Chemistry of Carbon Compounds, E. H. Rodd, Ed., Vol. Ib, p. 888, Elsevier Press Inc., New York (1952).

(27) K. W. Ratts and A. N. Yao: J. Org. Chem. 31, 1185 (1966).

(28) H. Nozaki, D. Tunemoto, Z. Morita, K. Nakamura, K. Watanabe, M. Takaku and K. Kondo: Tetrahedron 23,4279 (1967).

(29) D. R. Rayner, E. G. Miller, P. Bickart, A. J. Gordon and K. Mislow: J. Am. Chem. Soc. 88, 3138 (1966).

(30) D. L. Griffith and J. D. Roberts: J. Am. Chem. Soc. 87, 4089 (1965).

(31) W. Moffitt: Proc. Roy. Soc. (London) A200, 409 (1950).

(32) W. G. Penney and G. B. B. M. Sutherland: Trans.Faraday Soc. 30, 898 (1934); J. Chem. Phys. 2, 492 (1934).

(33) H. A. Bent: Chem. Rev. 61, 275 (1961).

(34) L. F. Fieser: Experiments in Organic Chemistry, 3rd Edition, p. 282. D. Heath and Co., Boston (1957).

(35) L. F. Fieser: Experiments in Organic Chemistry, 3rd Edition, p.283. D. Heath and Co., Boston (1957).

(36) E. D. Hughes and K. I. Kuriyan: J. Chem. Soc. 1609 (1935).

(37) (a) K. W. Ratts: Tetrahedron Letters, 4707 (1966).
  (b) A. Hochrainer and W. Silan: Monatsh. Chem. 97, 1477 (1966).
  (c) H. Nozaki, D. Tunemoto, K. Nakamura, K. Watanabe, M. Takaku and K. Kondo: Tetrahedron 23, 4279 (1967).

(38) D. W. J. Cruickshank: J. Chem. Soc. 5486 (1961).

(39) A. F. Cook and J. G. Moffatt: J. Am. Chem. Soc. 90, 740 (1968).

B29900